REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
February 2013	Viewgraph	February 2013- April 2013

4. TITLE AND SUBTITLE
Thermal Decomposition Mechanisms of Ionic Liquids by Direct Dynamics Simulations and Vacuum Ultraviolet Photoionization Mass Spectrometry

5a. CONTRACT NUMBER
FA9300-06-C-0023

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S. D. Chambreau, J. Liu, G. L. Vaghjiani, C. J. Koh, A. Golan, O. Kostko, S. R. Leone

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
23030423

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2013-042

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited. PA#13183

13. SUPPLEMENTARY NOTES
Viewgraph for the American Chemical Society Meeting, New Orleans, LA, 6-11 April 2013.

14. ABSTRACT

Due to the unusually high heats of vaporization of room-temperature ionic liquids (RTILs), volatilization of RTILs through thermal decomposition and vaporization of the decomposition products can be significant. In complex molecules like RTILs, use of chemical intuition to predict reaction pathways can prove unreliable, especially when the internal energy content is high. There may be concerted reactions that are difficult to predict, and once energy stored in the molecule begins to release, the system does not necessarily follow the minimum energy reaction path, i.e., the subsequent behavior is controlled by dynamics. A useful approach to treating such a system is quasi-classical, direct dynamics trajectory simulations, where the motion of the molecule is followed, allowing the molecule to "show us" what the preferred reaction pathways are. The direct dynamics method dispenses with the potential energy surface. Instead, it calculates the energies, force constants, and Hessian "on the fly" using quantum chemistry methods. This method becomes computationally attractive when the dimensionality of the system increases, particularly for RTILs, which typically contain 10 or more heavy atoms. Dynamics simulations allows the partitioning of the energy generated by exothermic reactions into vibrational, rotational, and translational degrees of freedom, thereby increasing the chance of locating new reaction pathways in the system. In addition, by following the variation of the potential energy during the trajectory rather than relying on intuition, we can identify better geometries for TS searching. Results obtained from these direct dynamics simulations are compared to and consistent with the gaseous products detected experimentally via tunable vacuum ultraviolet photoionization mass spectrometry performed at the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source. The likely reaction mechanisms in the thermal decomposition of RTILs are discussed in this work.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Tommy Hawkins
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	44	**19b. TELEPHONE NO** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			661-525-5449

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Thermal decomposition mechanisms of ionic liquids by direct dynamics simulations and vacuum ultraviolet photoionization mass spectrometry

Steve Chambreau

American Chemical Society Spring National Meeting
New Orleans, Louisiana
April 10, 2013

ERC, Inc.
Aerospace Systems Directorate
Propellants Branch
Air Force Research Laboratory
AFRL/RQRP
10 E Saturn Blvd
Edwards AFB, CA 93524

Tel: 661 275 6176
Fax: 661 275 5471
Email: steven.chambreau.ctr@edwards.af.mil

Outline

- Direct dynamics and RRKM modeling of:
  - 1,5-dinitrobiuret (DNB) pyrolysis.
  - $EMIM^+dca^-$, $EMMIM^+dca^-$
- IL vapor studies:
  - Photoionization of vaporized ILs.
- IL aerosols + HNO_3:
  - Diffusion-limited reactivity: MM
- QM/MM reactive scattering:
  - hyperthermal $O(^3P)$ off IL surface

What is *hypergolicity*??!

J. Phys. Chem. A, **2008**, *112* (34), pp 7816–7824
DOI: 10.1021/jp8038175

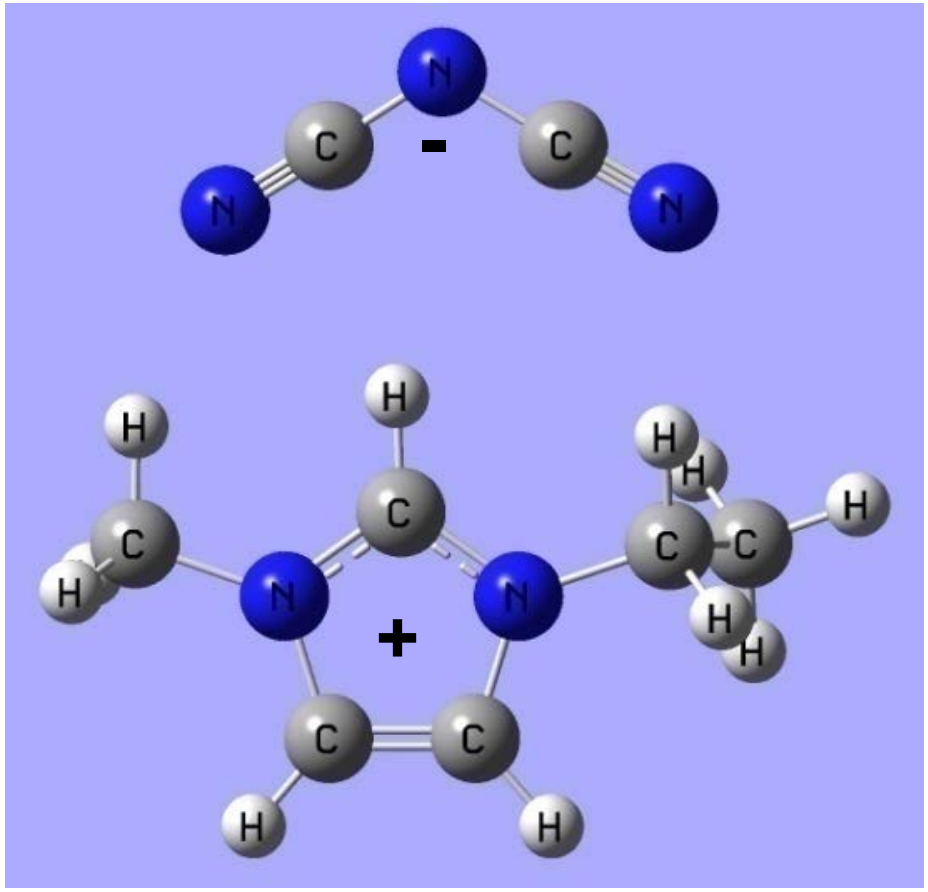
Motivation

- Replacement for monomethylhydrazine (MMH) + N_2O_4 (highly volatile and toxic!!)

Ionic Liquids

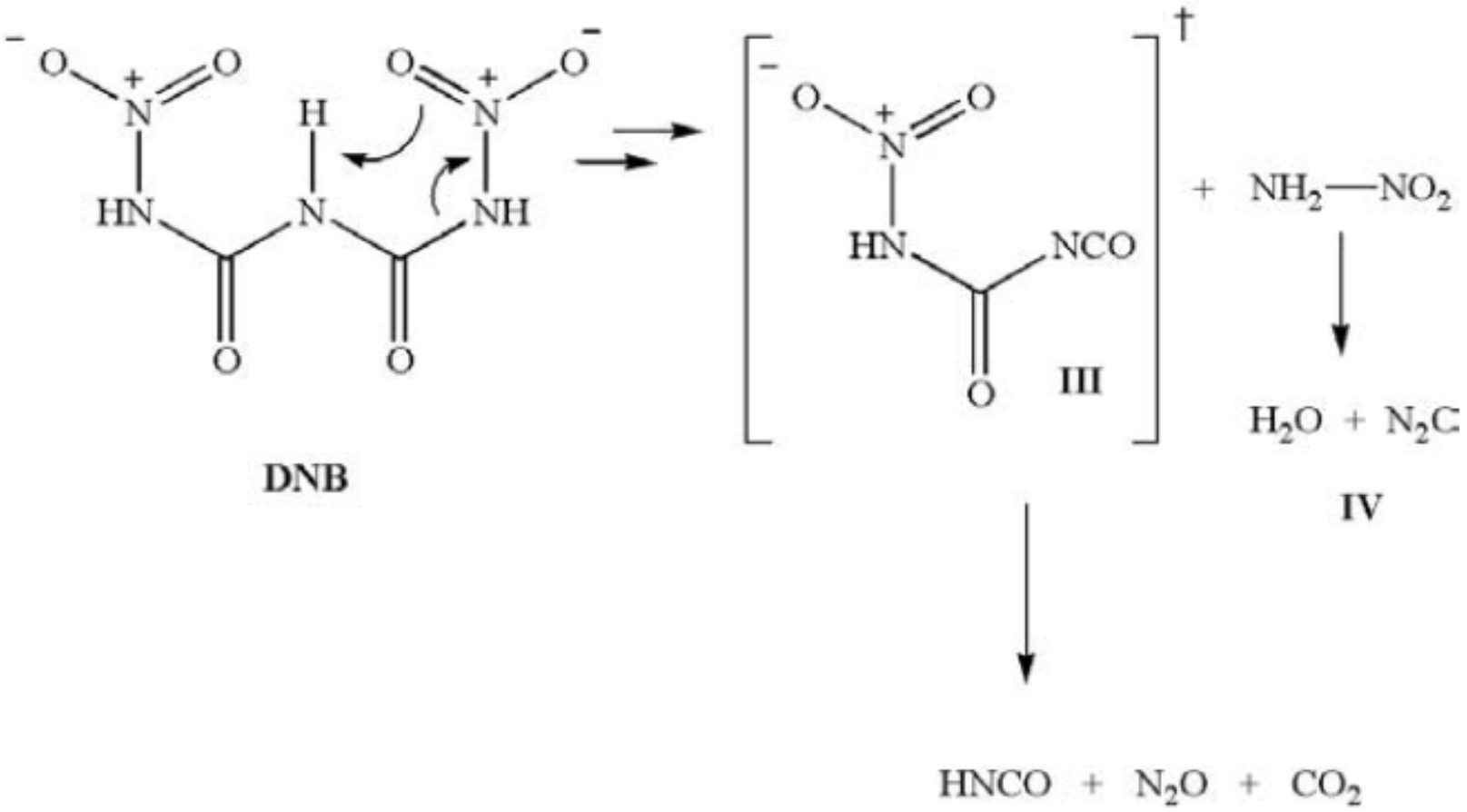
- Molten salts with m.p. ≤100 °C.
- Asymmetric ions with diffuse charge distributions.
- C^+A^- : 10^{18} possible combinations of cations and anions.

Background

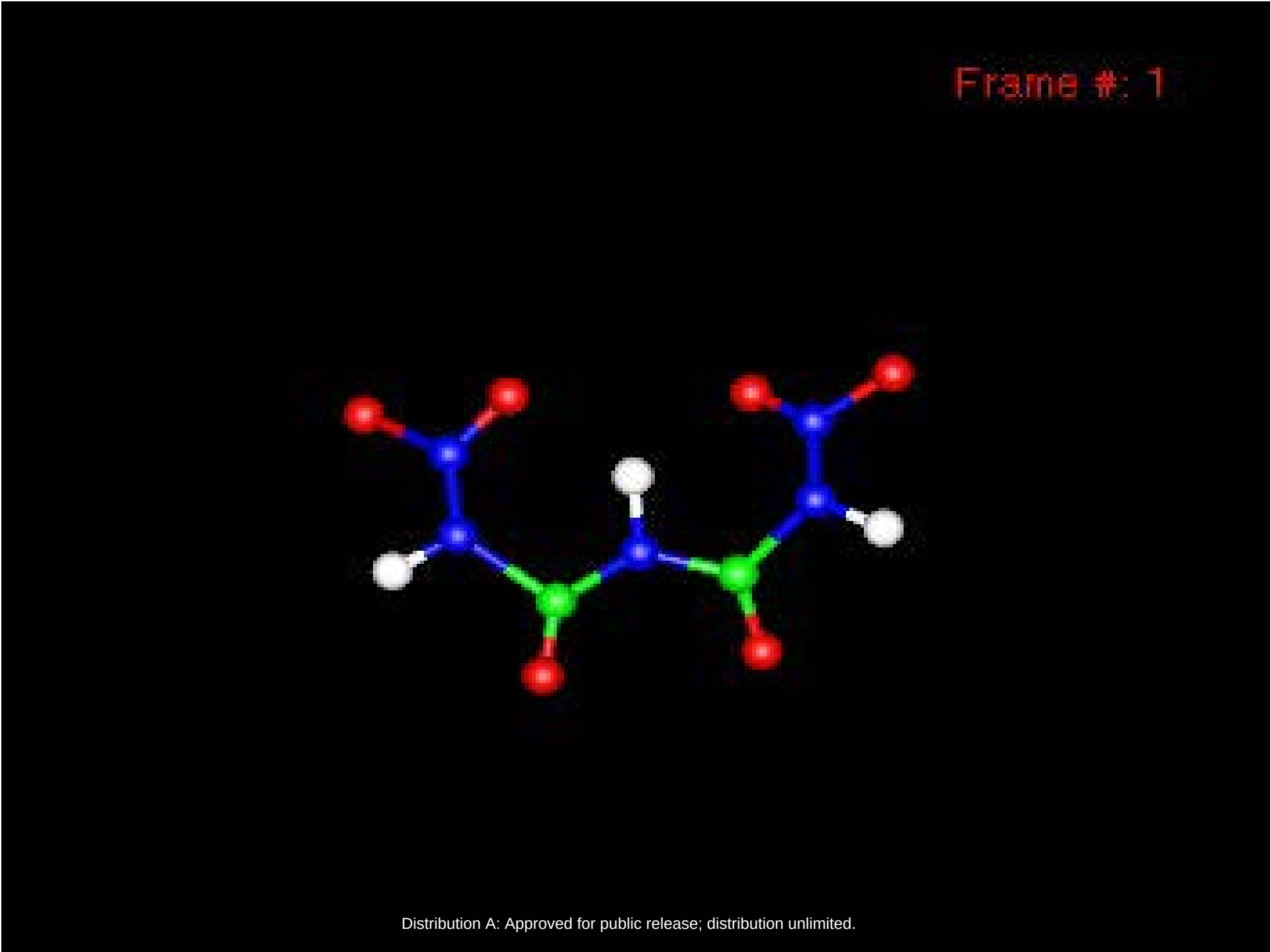


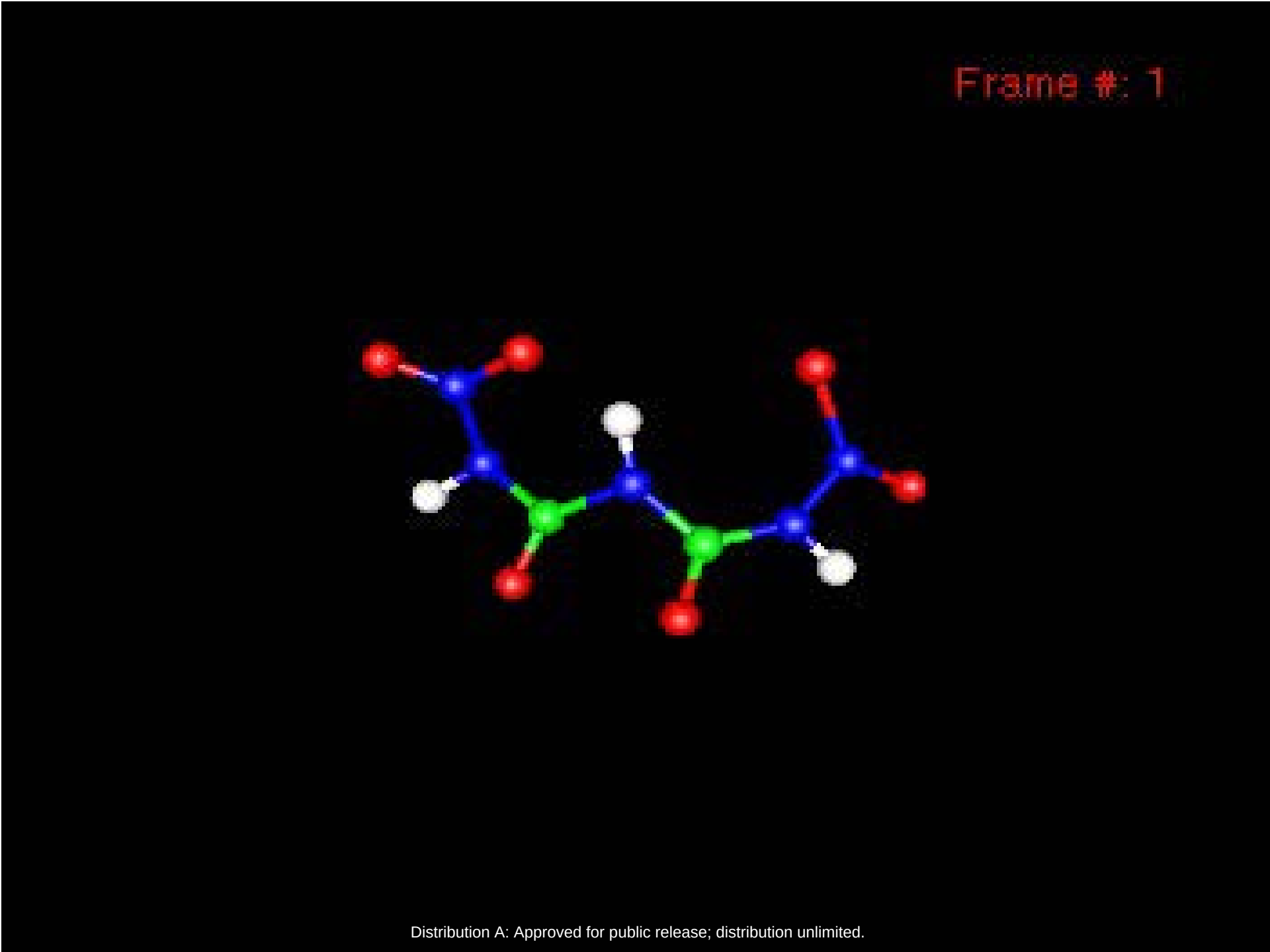
- Dicyanamide-based RTILs first hypergolic ILs discovered with HNO_3.

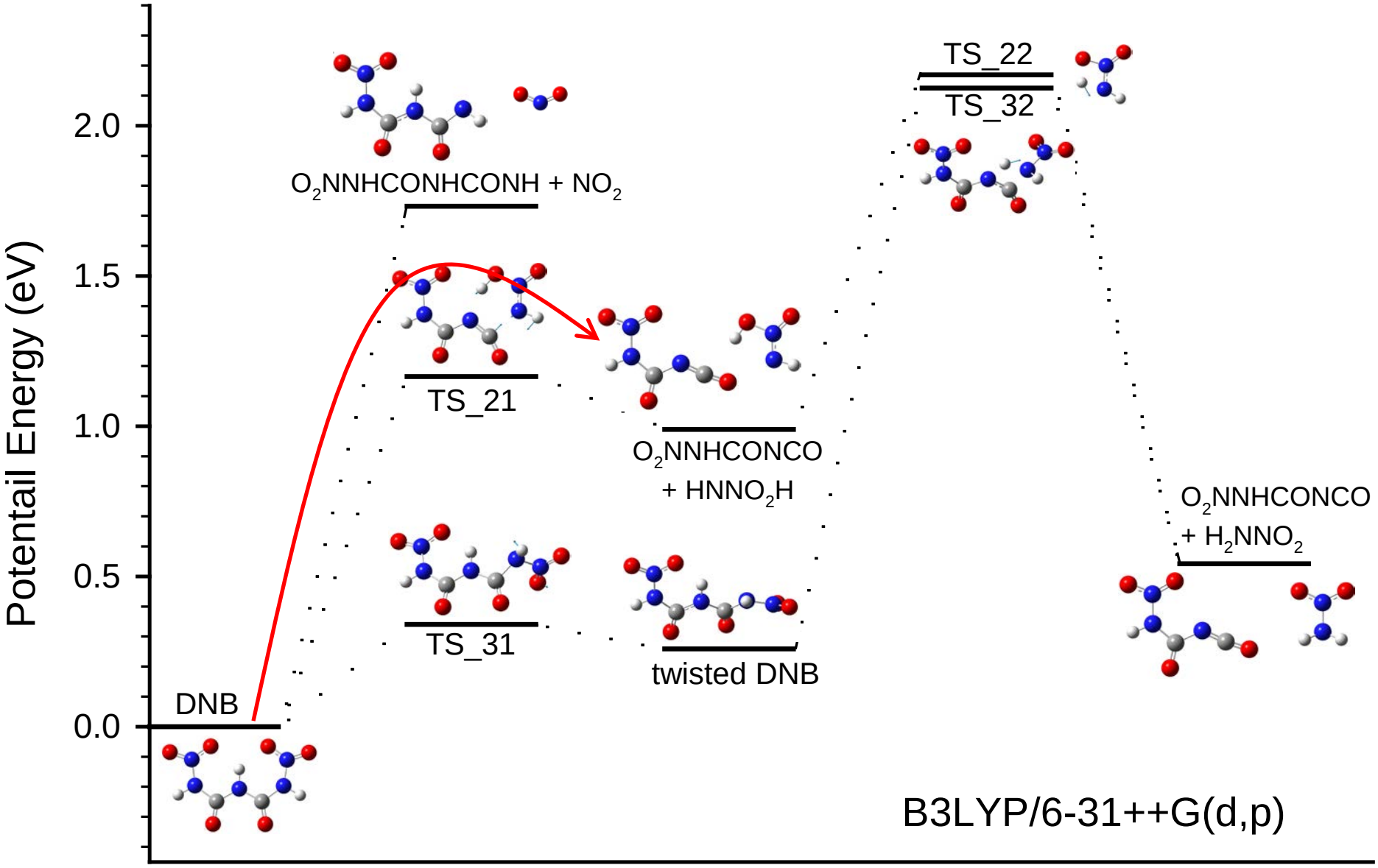
Gas Phase Decomposition of DNB



Geith, J., Holl, G., Klapötke, T. M., Weigland, J. J., *Combust. Flame*, **2004**, *139*, 358-366







RRKM Results

Temp / K	750	1000	1250	1500	1750	2000
			density of states ($1/cm^{-1}$)			
DNB	1.95×10^{18}	2.34×10^{22}	5.98×10^{25}	4.94×10^{28}	1.71×10^{31}	2.92×10^{33}
twisted DNB	1.90×10^{18}	2.33×10^{22}	6.04×10^{25}	5.04×10^{28}	1.75×10^{31}	3.02×10^{33}
			unimolecular rates (s^{-1}) [a]			
k_1	0 (0)	0.6 (3.6)	1.8×10^{4} (1.8×10^{5})	2.1×10^{6} (2.7×10^{7})	3.9×10^{7} (5.8×10^{8})	2.9×10^{8} (4.7×10^{9})
k_2	8.5	9.7×10^{5}	7.9×10^{7}	1.0×10^{9}	5.5×10^{9}	1.8×10^{10}
k_{31}	3.4×10^{9}	1.5×10^{10}	3.5×10^{10}	6.0×10^{10}	8.8×10^{10}	1.2×10^{11}
k_{-31}	2.4×10^{11}	3.2×10^{11}	3.8×10^{11}	4.4×10^{11}	4.8×10^{11}	5.1×10^{11}
k_{32}	0	1.5×10^{-2}	2.1×10^{4}	7.9×10^{6}	2.9×10^{8}	3.4×10^{9}
			branching ratios (%) [a]			
path 1	0	0	0 (0.3)	0.2 (2.6)	0.7 (9.1)	1.3 (18.0)
path 2	100	100	100 (99.7)	99.0 (96.7)	94.3 (86.3)	83.3 (69.2)
path 3	0	0	0	0.8 (0.8)	5.0 (4.5)	15.4 (12.8)

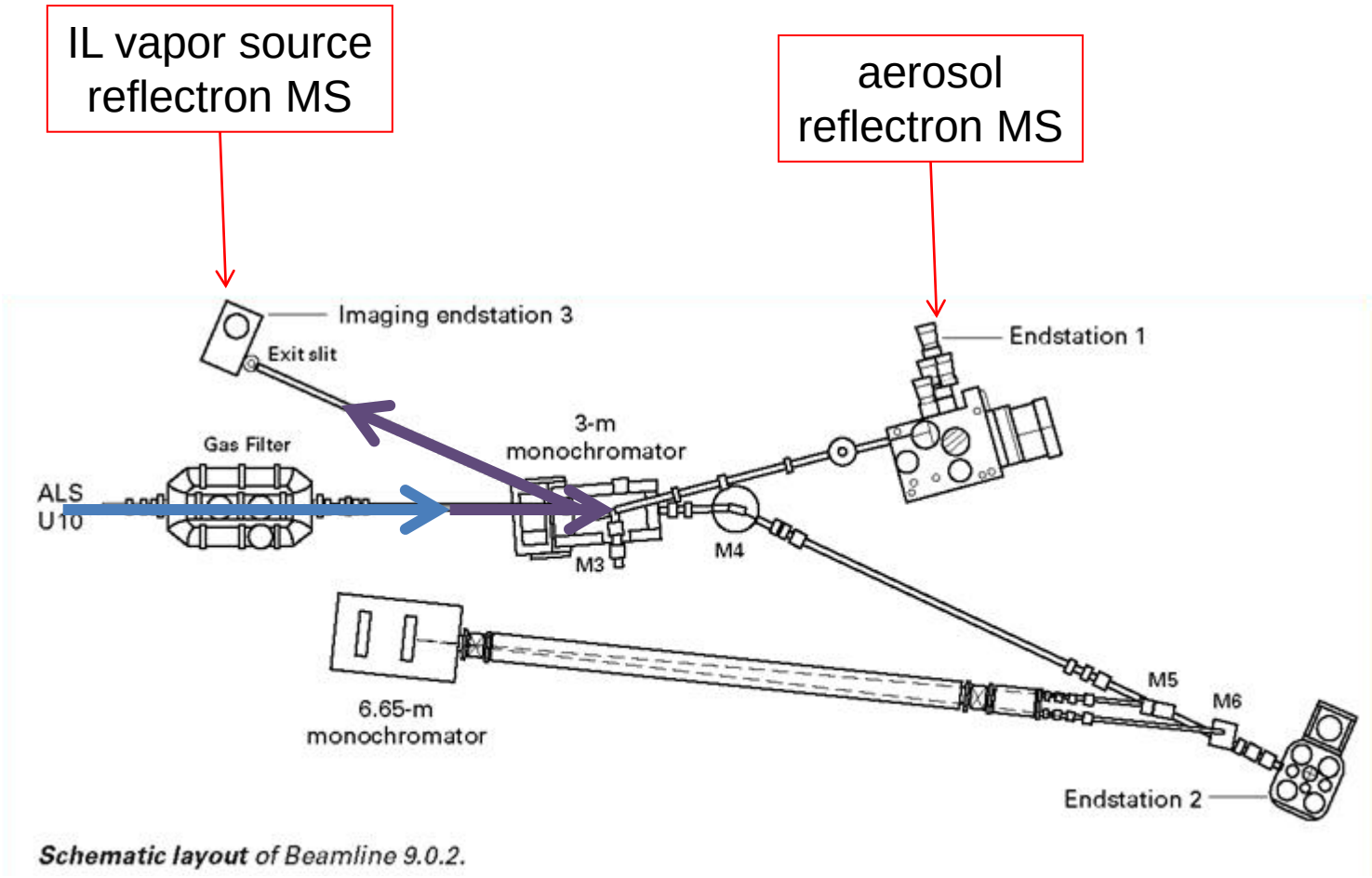
() = loose transition state for path 1

IL Vaporization

- Strasser, Armstong, indicate ion pairs by detection of intact cation:[1]
  - **Ionic Liquid + Δ → $C^+A^-_{(g)}$**
  - **$C^+A^-_{(g)}$ + hv → C^+A + e^- → C^+ + A + e^-**
- Kelkar and Maginn: ion pairs more energetically favorable than clusters of ion pairs and non-neutral clusters.[2]

[1] *J. Phys. Chem. A*, 2007, **111**, 3191-3195; *PCCP*, 2007, **9**, 982-990.
[2] *J. Phys. Chem. B*, 2007, **111**, 9424-9427.

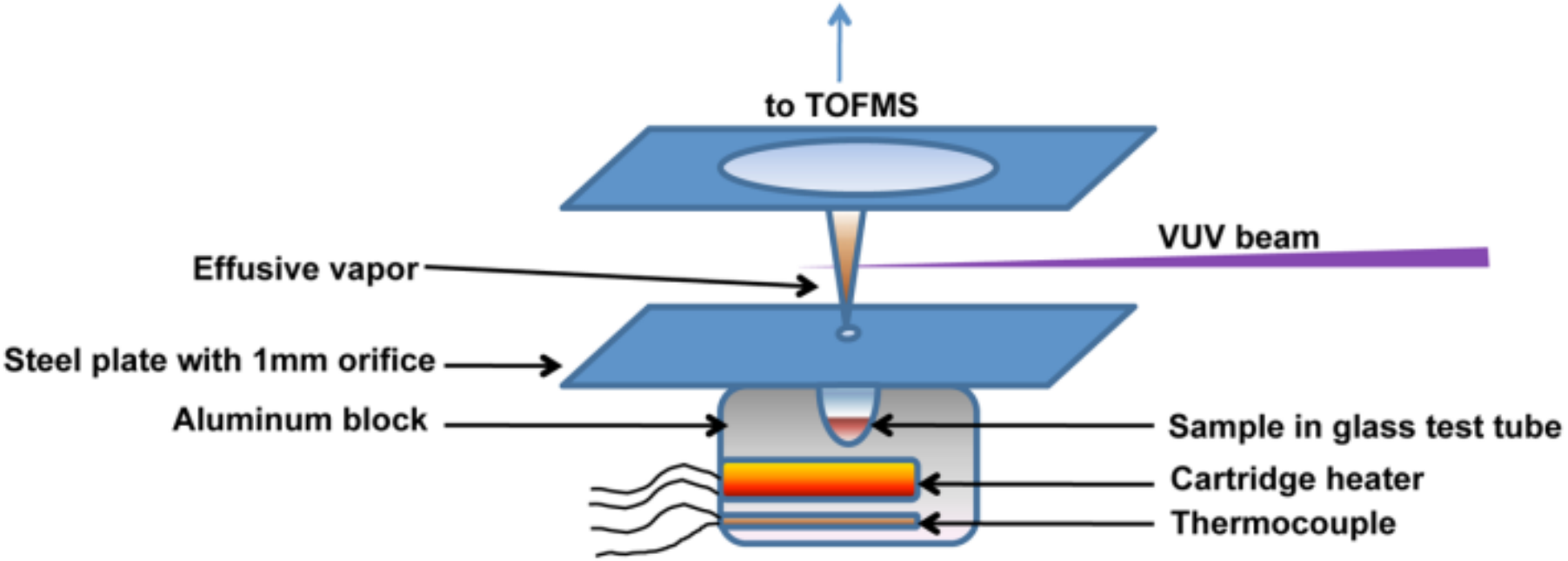
ALS: Chemical Dynamics Beamline

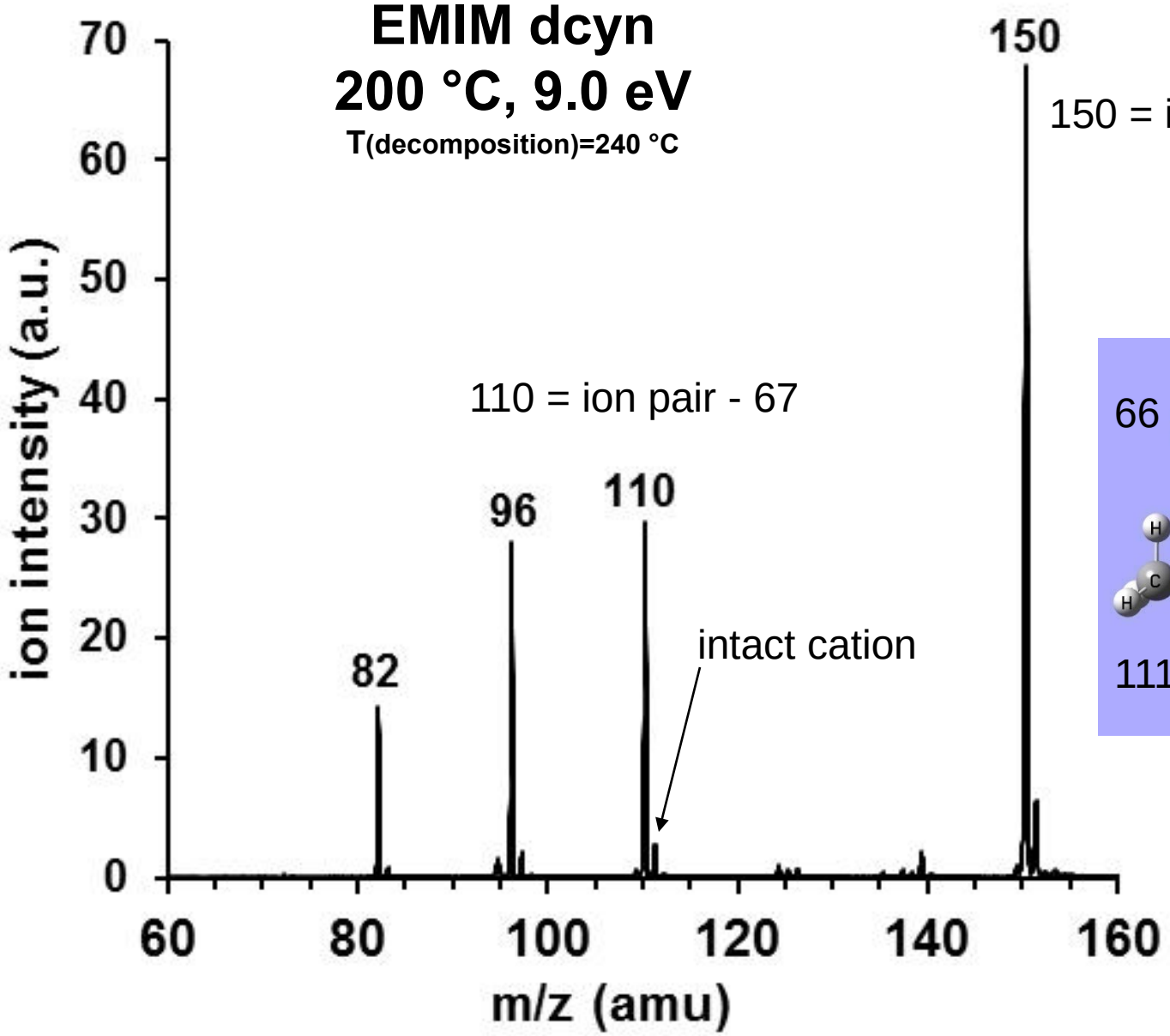


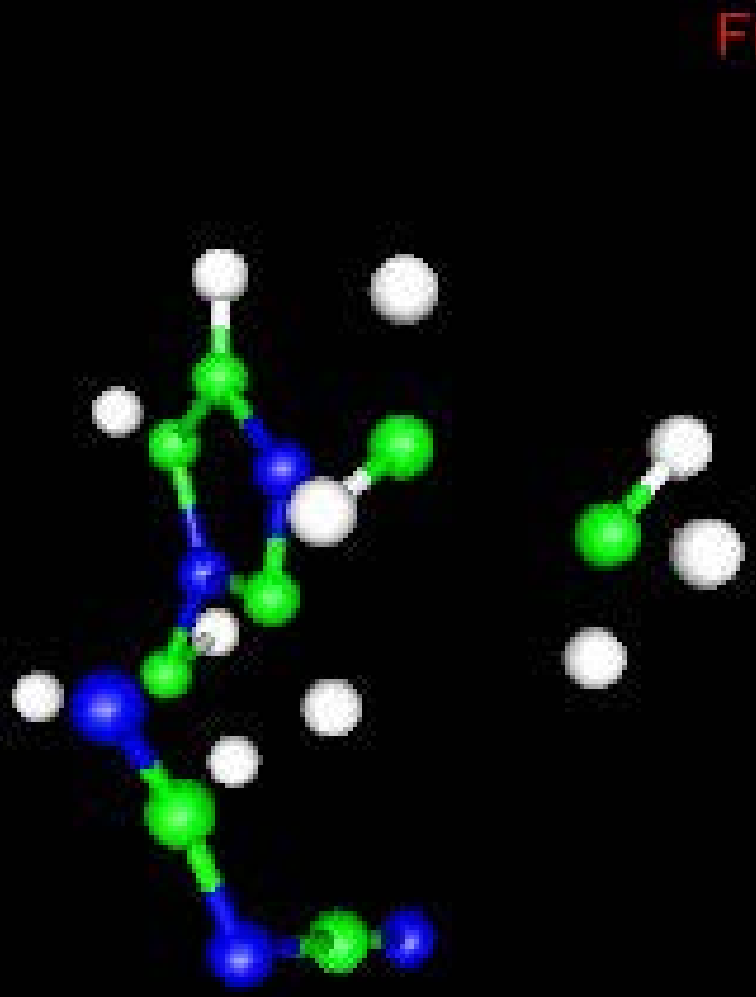
7.4-15.0 eV photons, 0.025 eV resolution

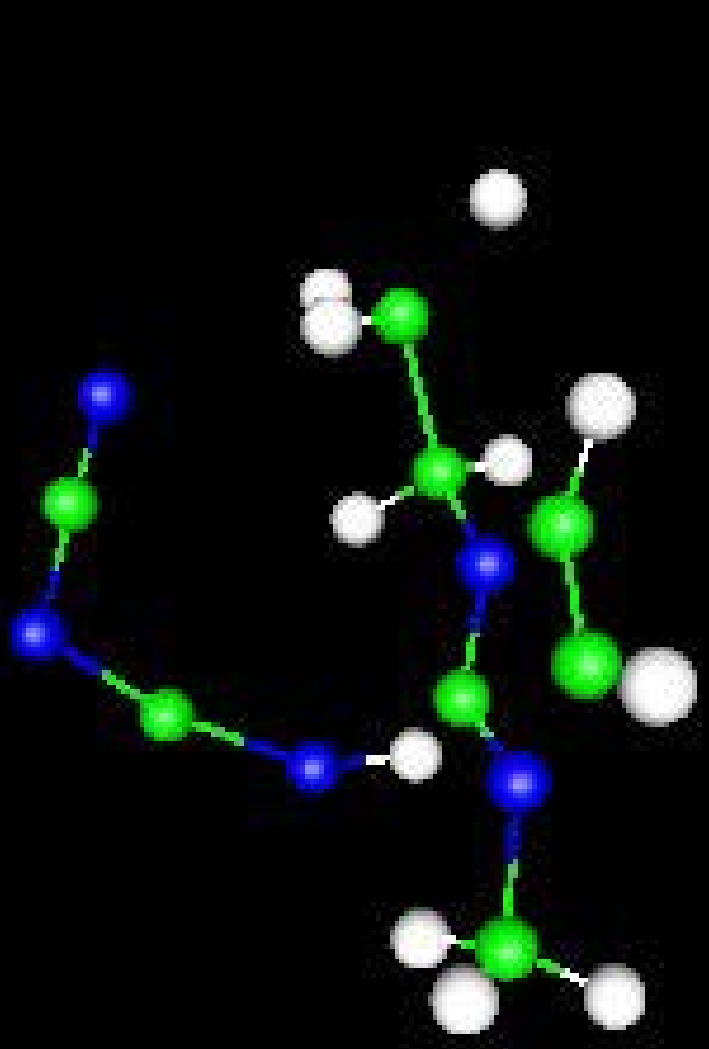
Experimental

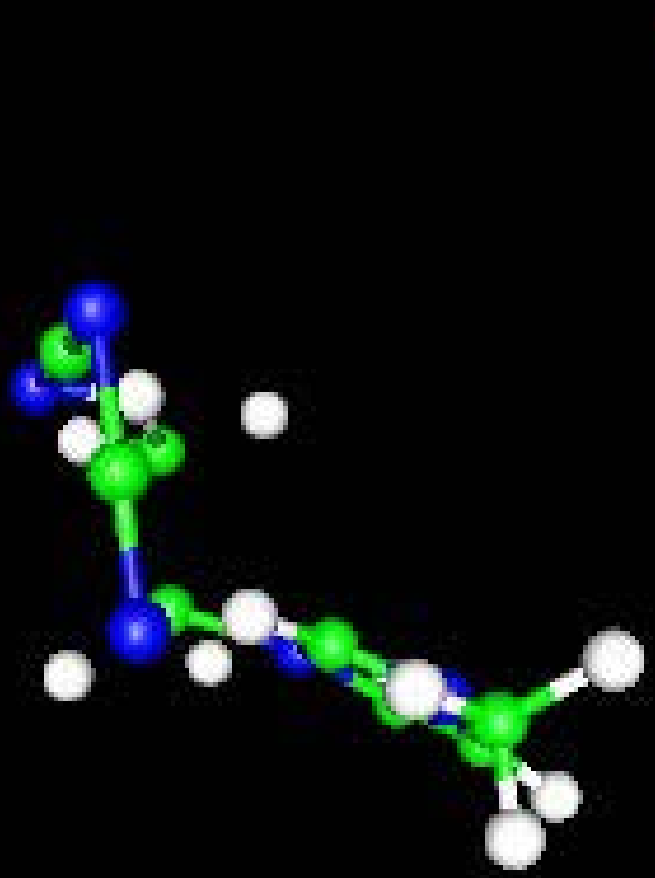
IL effusive source:









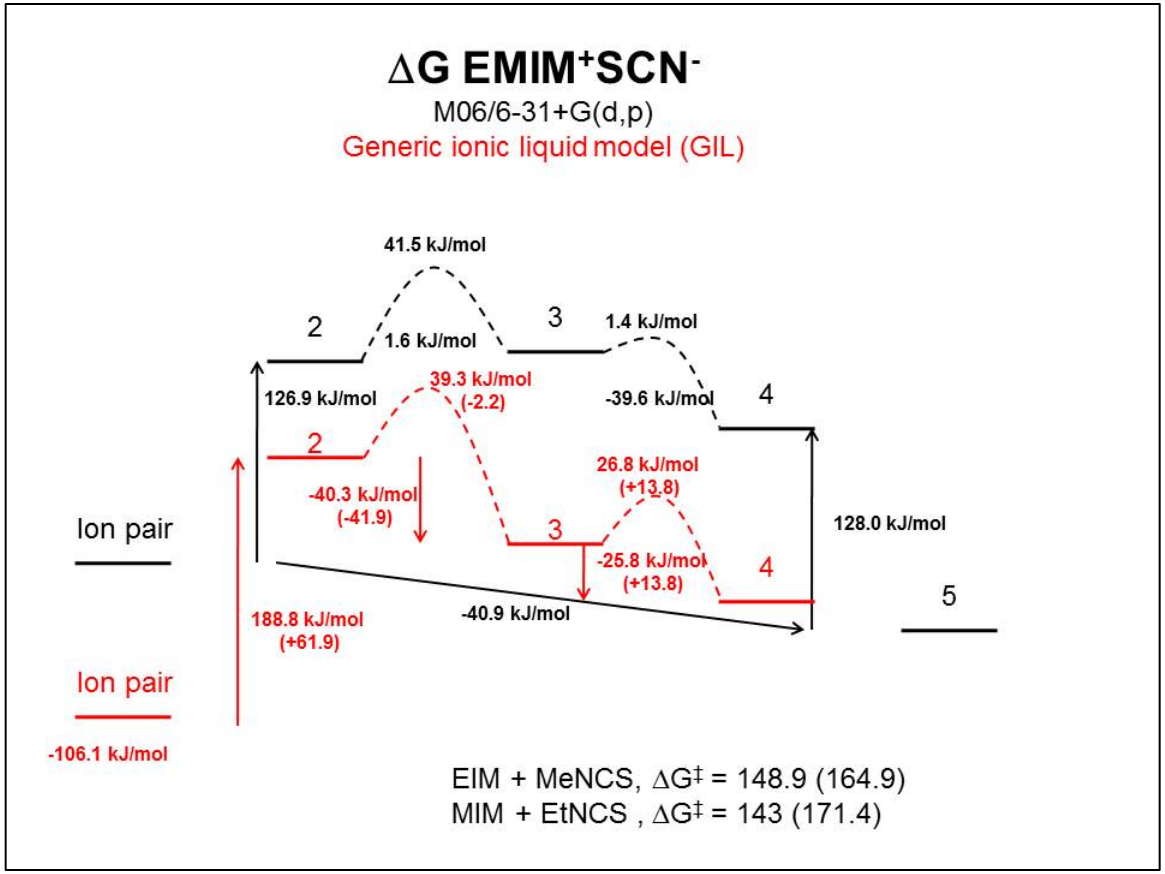


$EMIM^{+}dca^{-}$ MD results

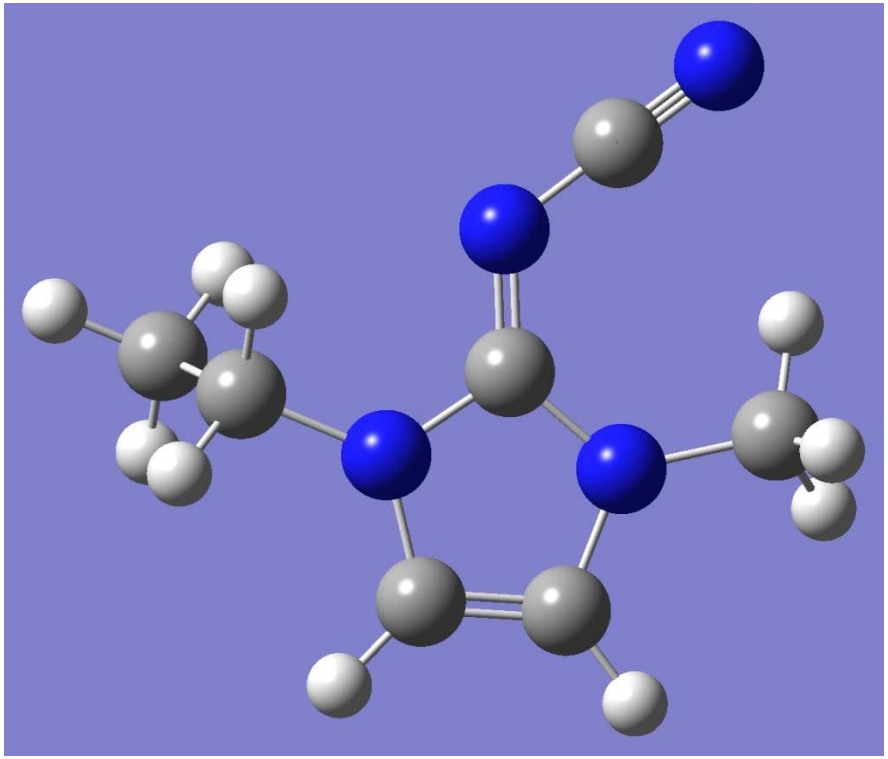
MD reaction	# of trajectories	branching ratio (%)
C2 H+ xfer to dca (term)	16	25
C2H5 dissoc	11	17
NCN + CN	8	13
dca dissoc	4	6
NR	4	6
dca abstract H from CH3 --> Hdca (term)	3	5
C2 H+ <-> dca (central)	2	3
CH3 dissoc	2	3
Et: CH3CH2- + dca --> CH2CH2 + Hdca (term)	2	3
H2 elim from -CH3	2	3
NCN-CN elongation	2	3
-C2H5 + dca <--> -C2H4 + Hdca	1	2
C2H5 abstraction by dca (term)	1	2
C2H5 and dca dissoc	1	2
C4H xfer to N3 and elim HC4C5	1	2
CH3 abstraction by dca (central)	1	2
CH3 abstraction by dca (term)	1	2
Et: H2 + dca --> HCN + HNCN	1	2
total=	63	

PCM Model for ILs

- Truhlar: SMD-GIL (generic ionic liquid)*
  - benchmark to experimental ΔG_{solv} for ILs.



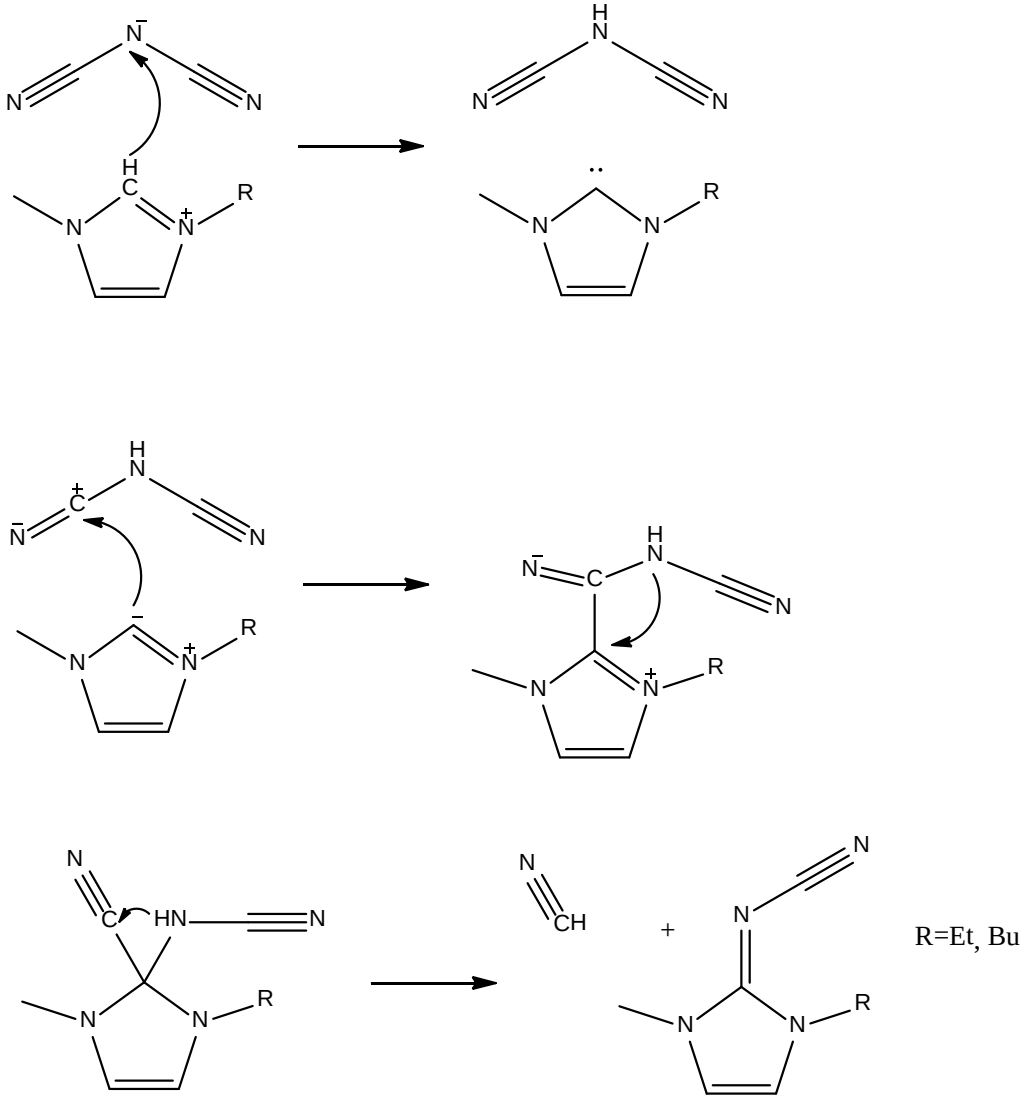
*J. Phys. Chem. B **2012**, 116, 9122−9129

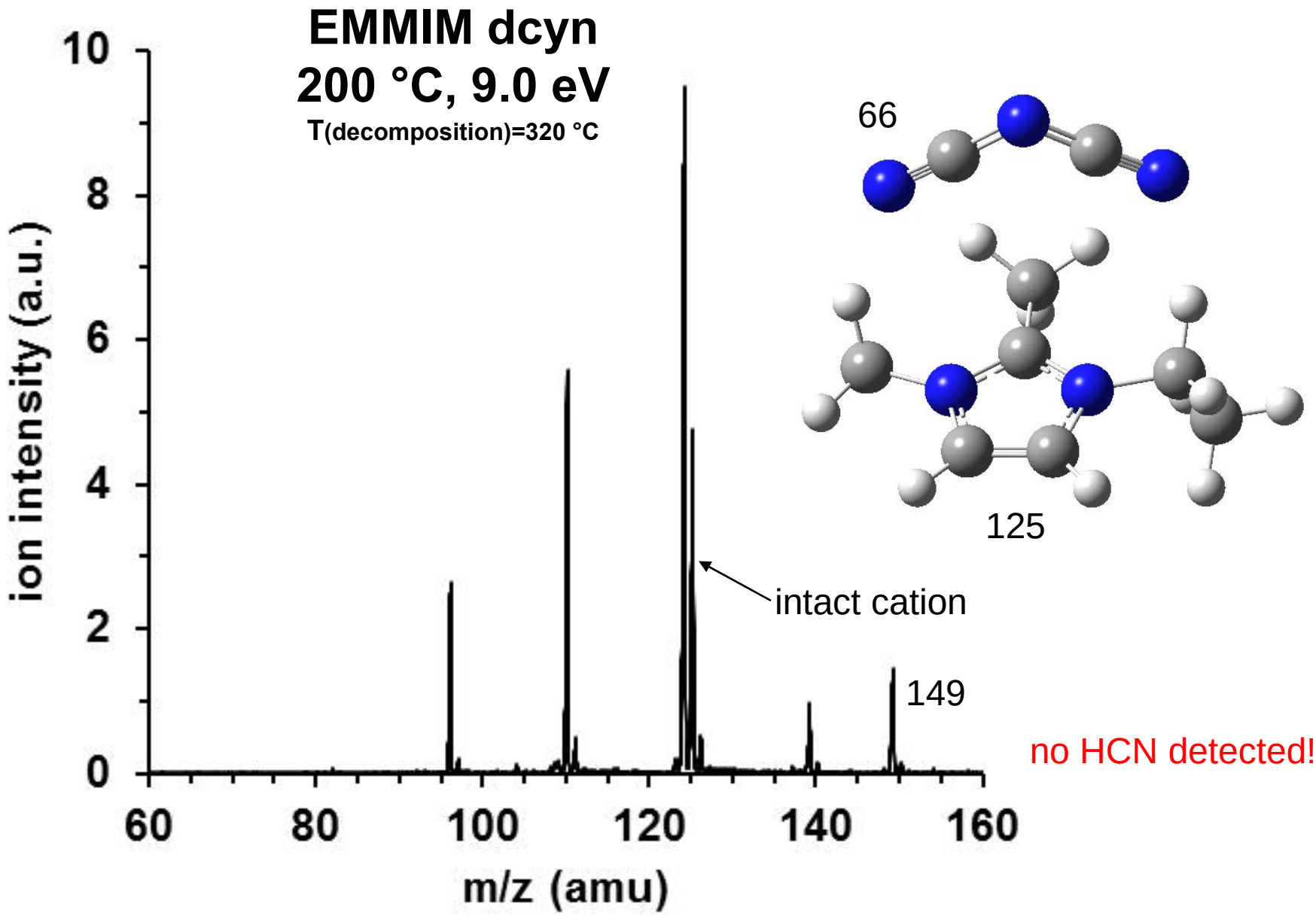


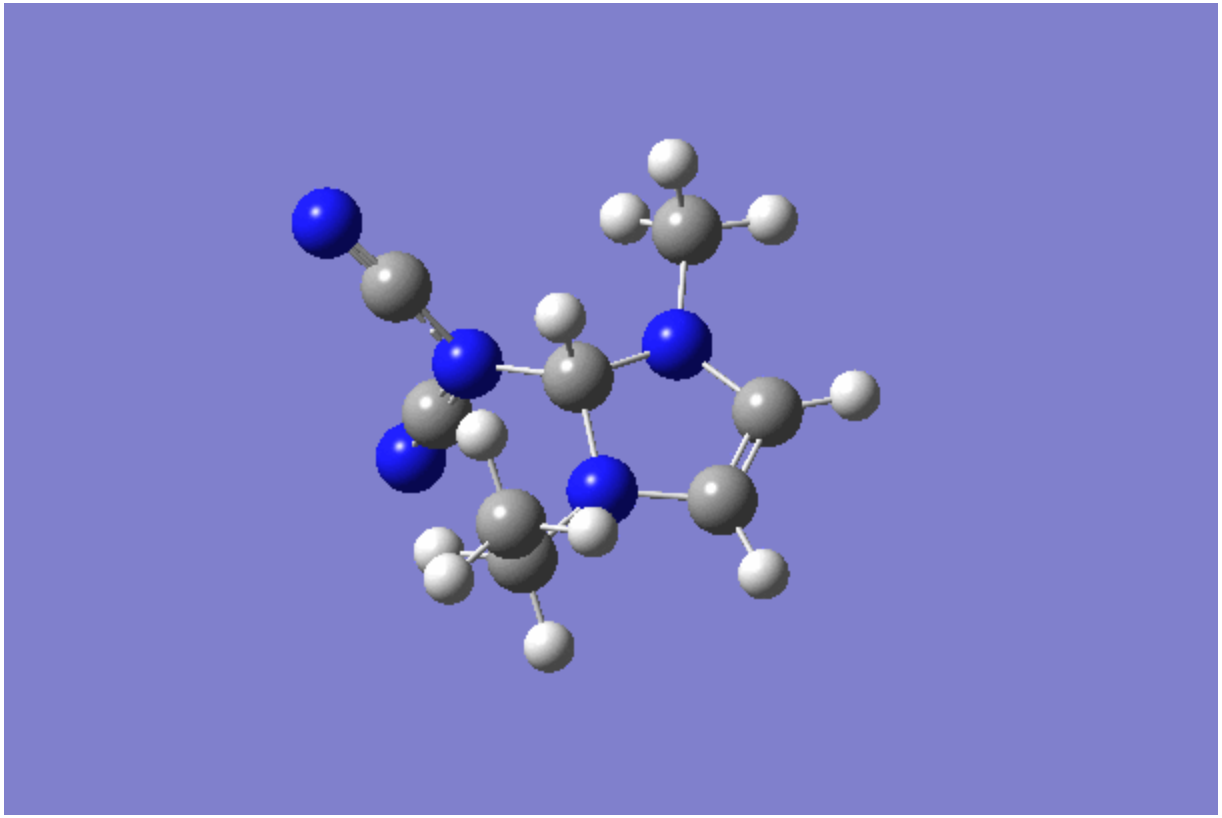
+ HCN

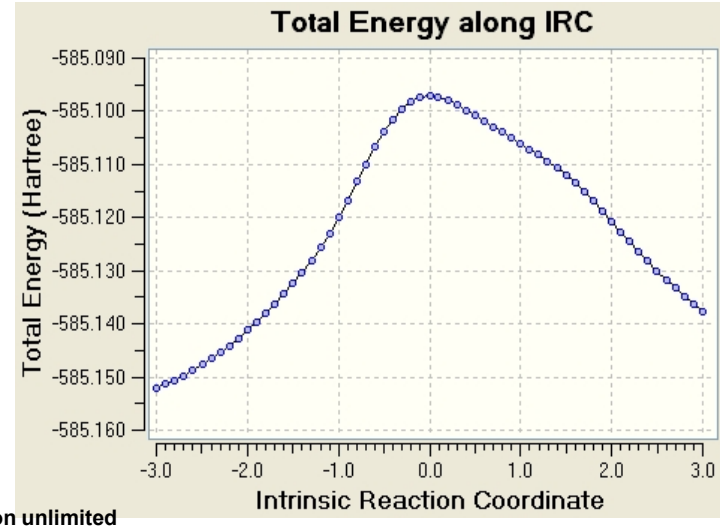
Mass 150
=(111-1) + 40

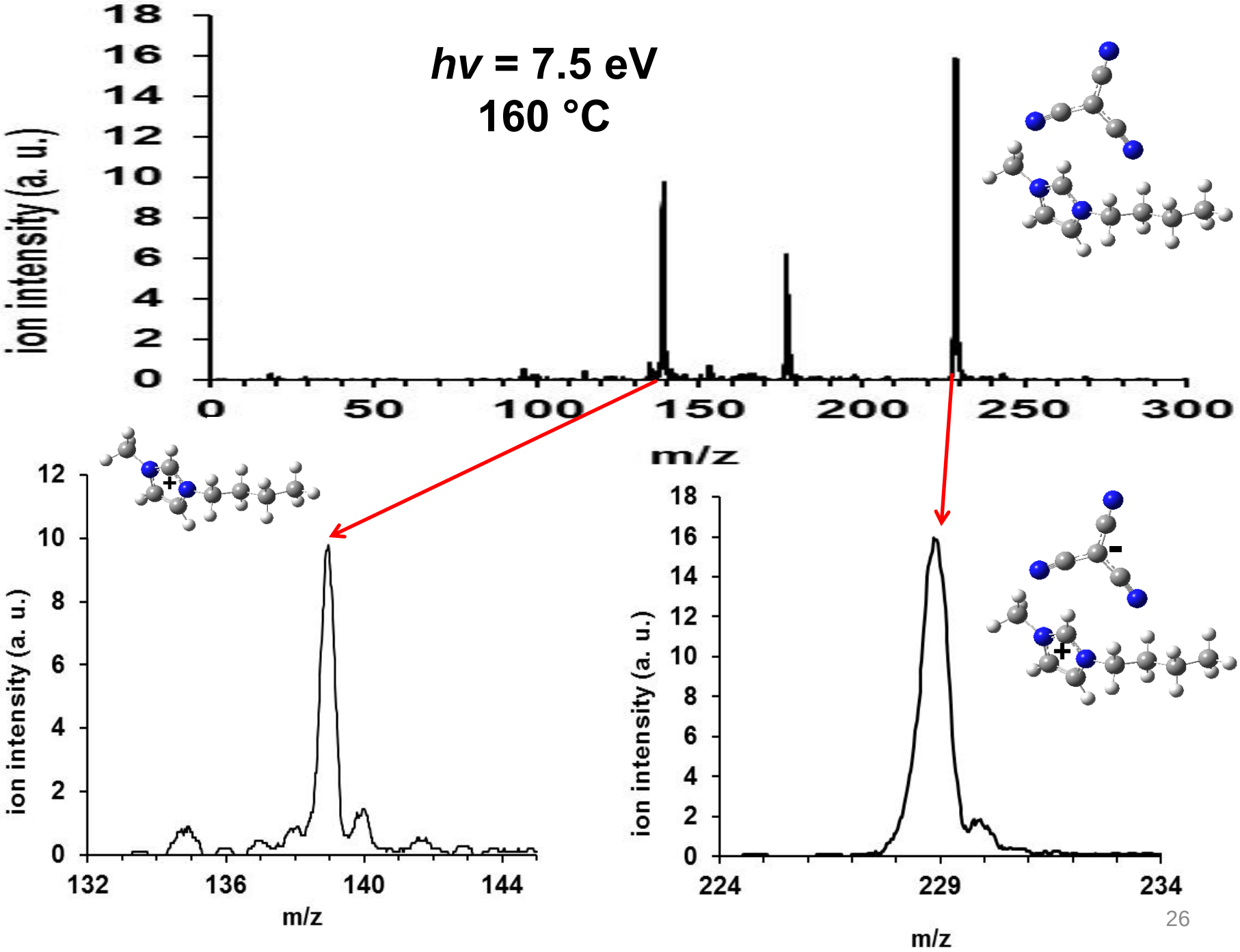
addition-elimination mechanism



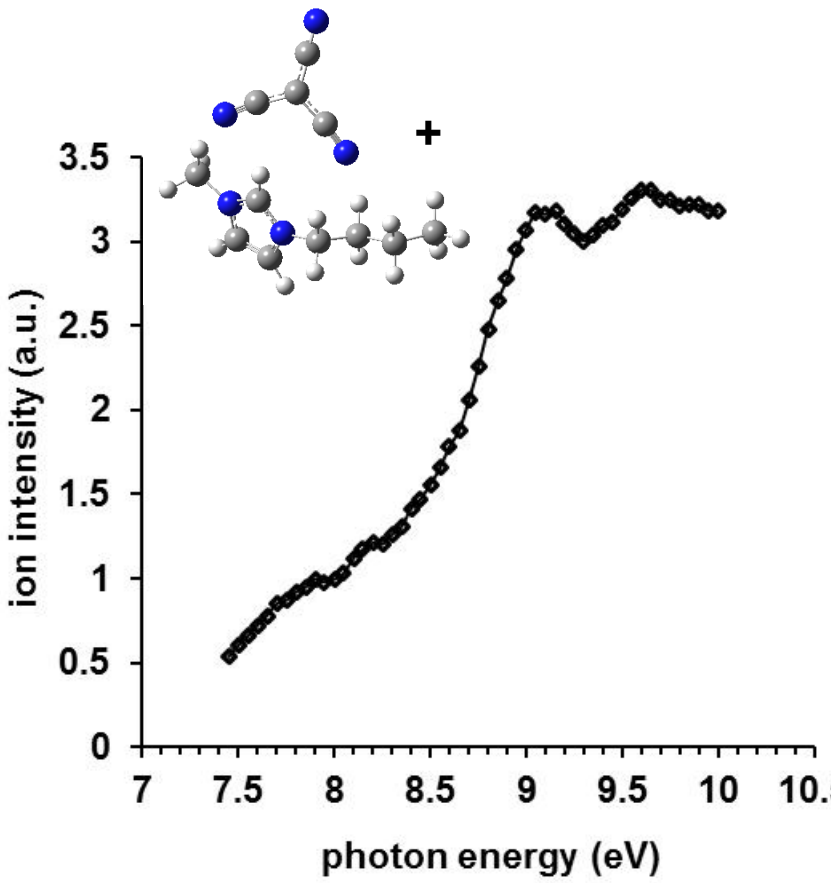


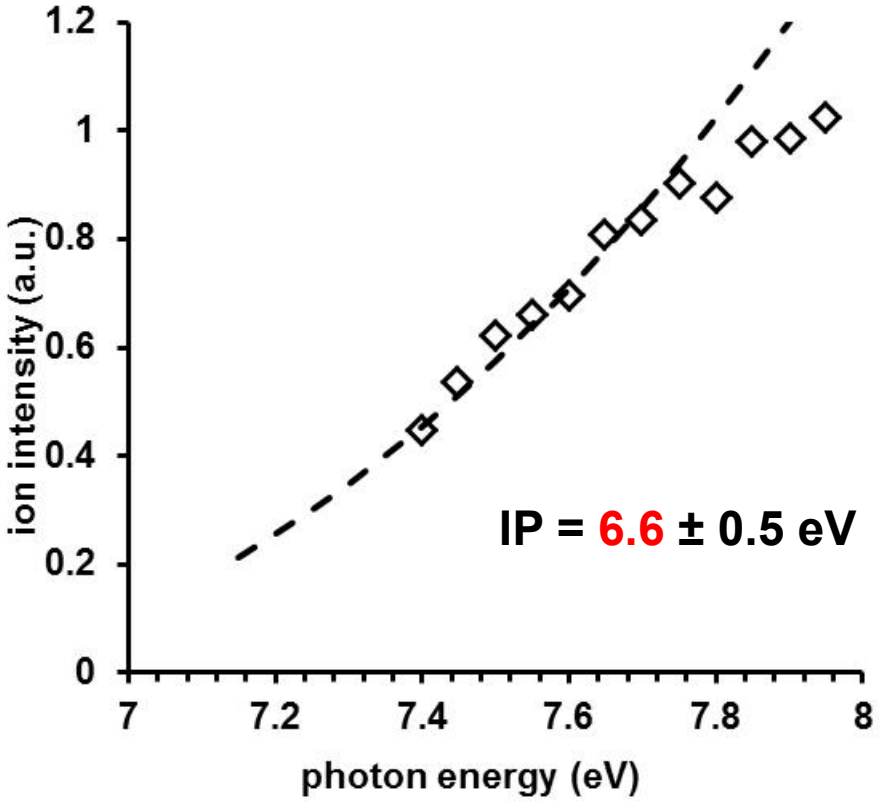





hν = 7.5 eV
160 °C
ion intensity (a. u.)
m/z
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250
300
ion intensity (a. u.)
m/z
132
136
140
144
ion intensity (a. u.)
m/z
224
229
234

photoionization efficiency of ion pair





J. Phys. Chem. Lett., **3**, 2910 (2012)

IP (M06/6-31+G(d,p))
7.3 ± 0.2 eV

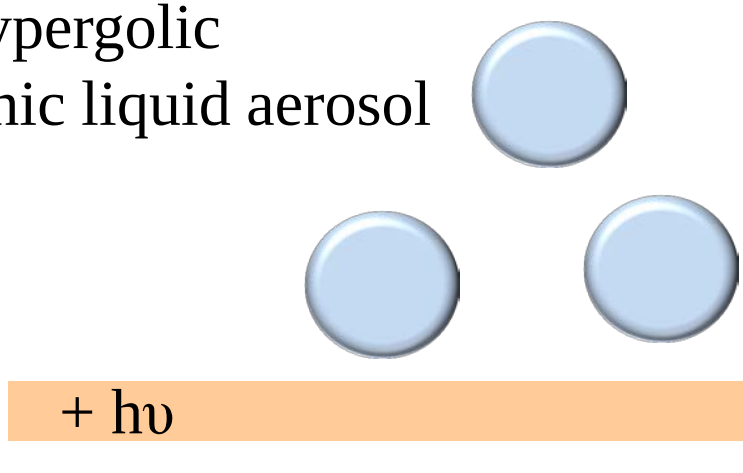
Aerosol reactivity

- RTILs very low vapor:
  - Aerosols are liquid droplets suspended in gas phase.

Monitoring isolated ion pairs

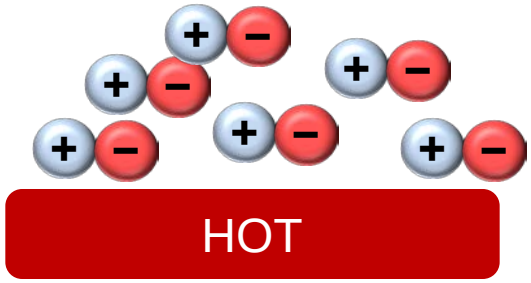
- Use it **to study reaction kinetics** of ‘hypergolic ionic liquid reaction with an oxidizer’

Hypergolic
Ionic liquid aerosol



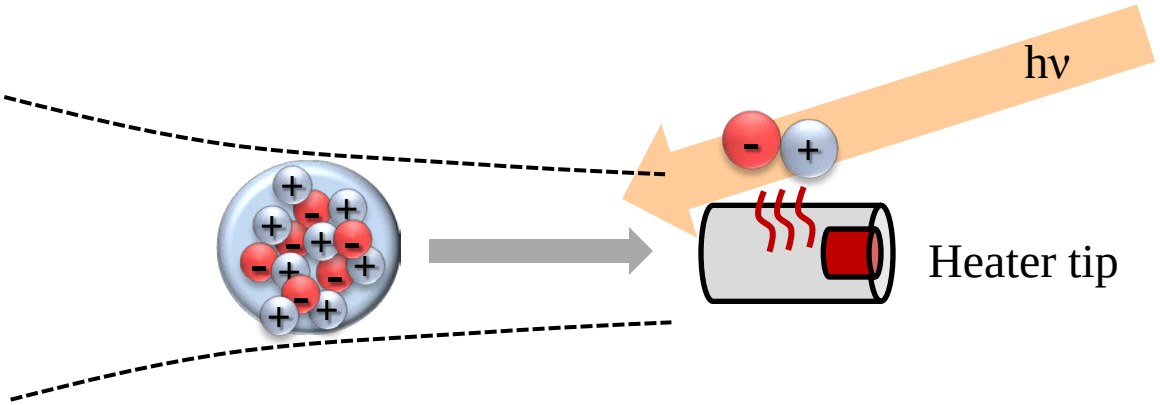
Hypergolic
Ionic liquid aerosol ‘reacted’

Reaction dynamics and kinetics



C. J. Koh, et al., *Soft ionization of thermally evaporated hypergolic ionic liquid aerosols* , J. Phys. Chem. **115**, 4630 (2011).

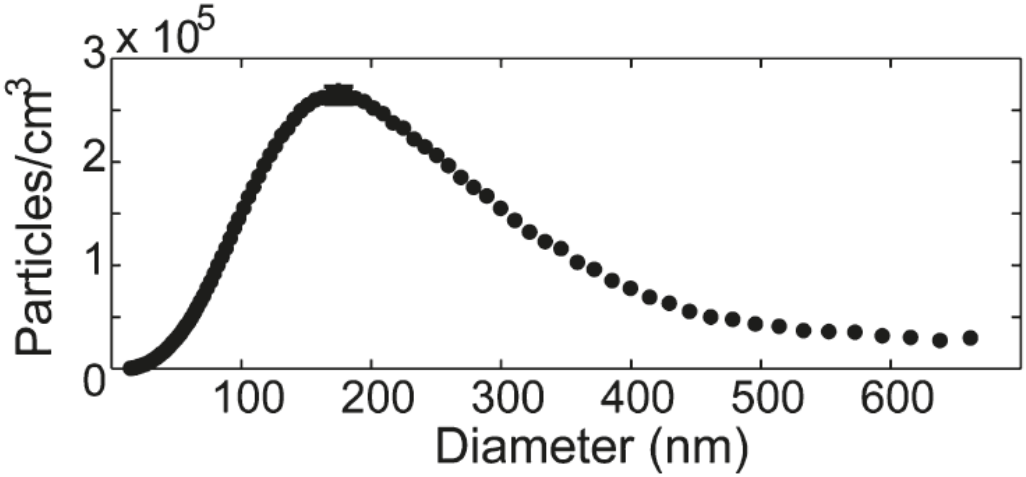
Ionic liquid aerosol generation



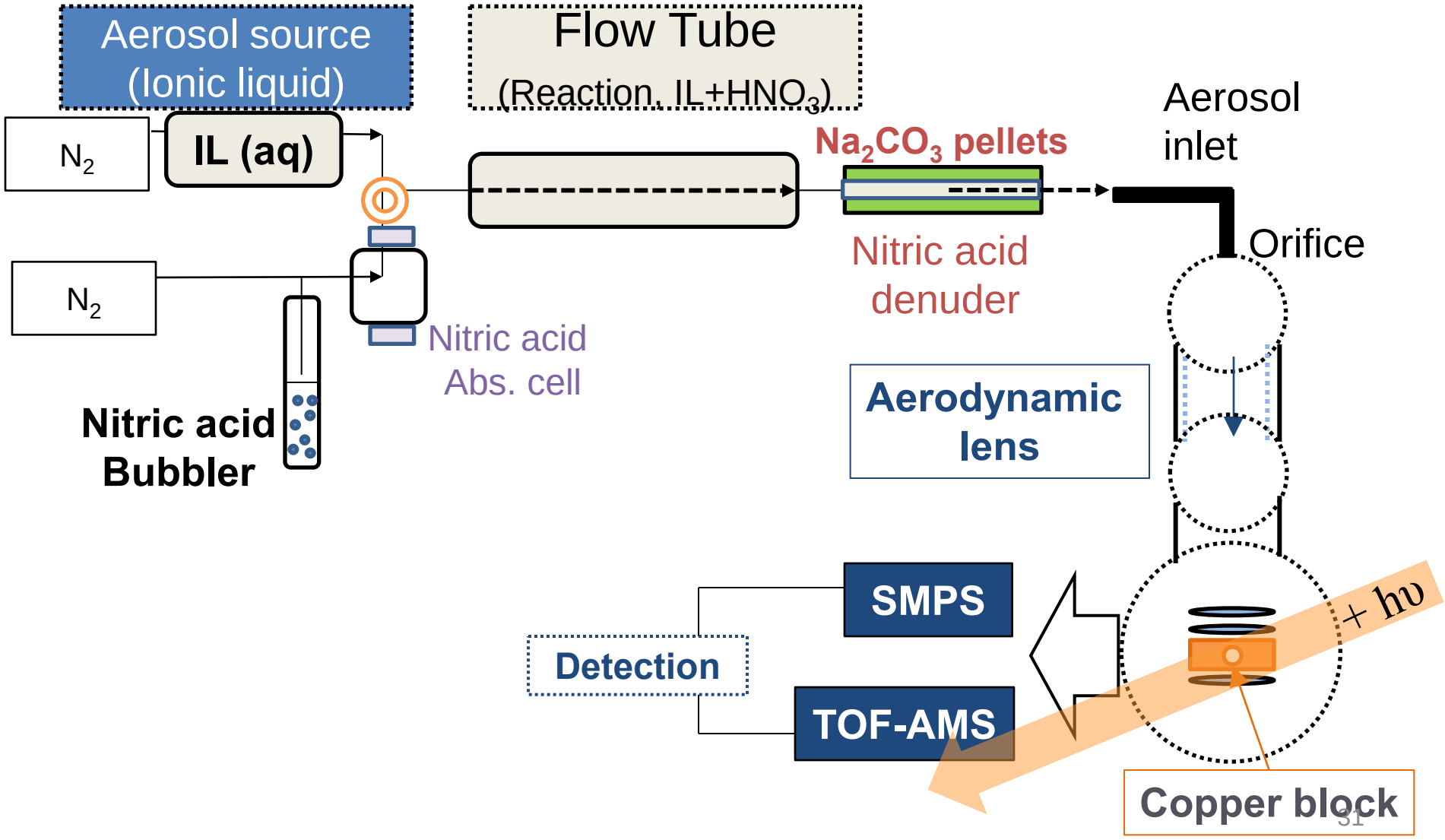
- Tunable light source

Hypergolic Ionic liquid aerosol

- size distribution

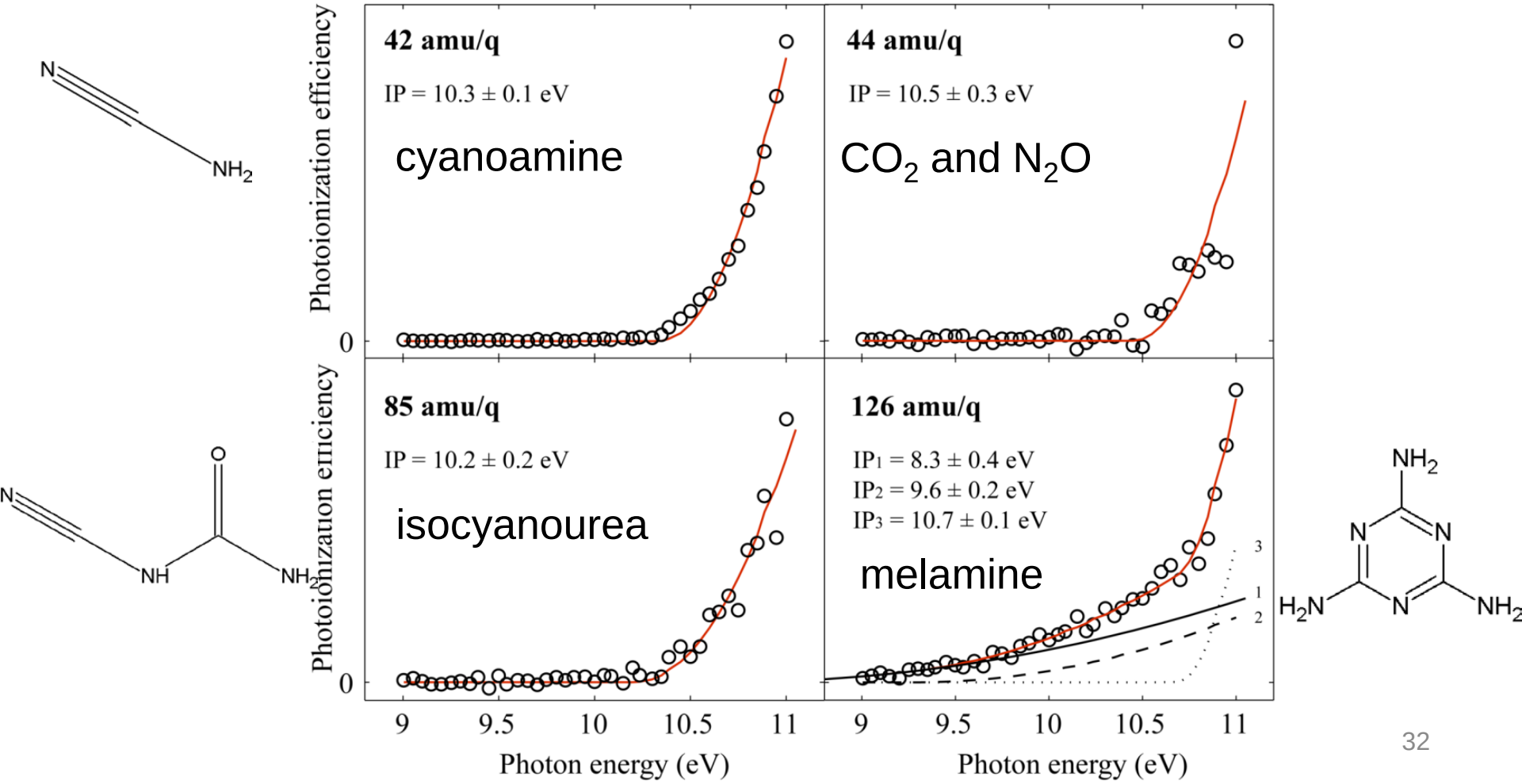


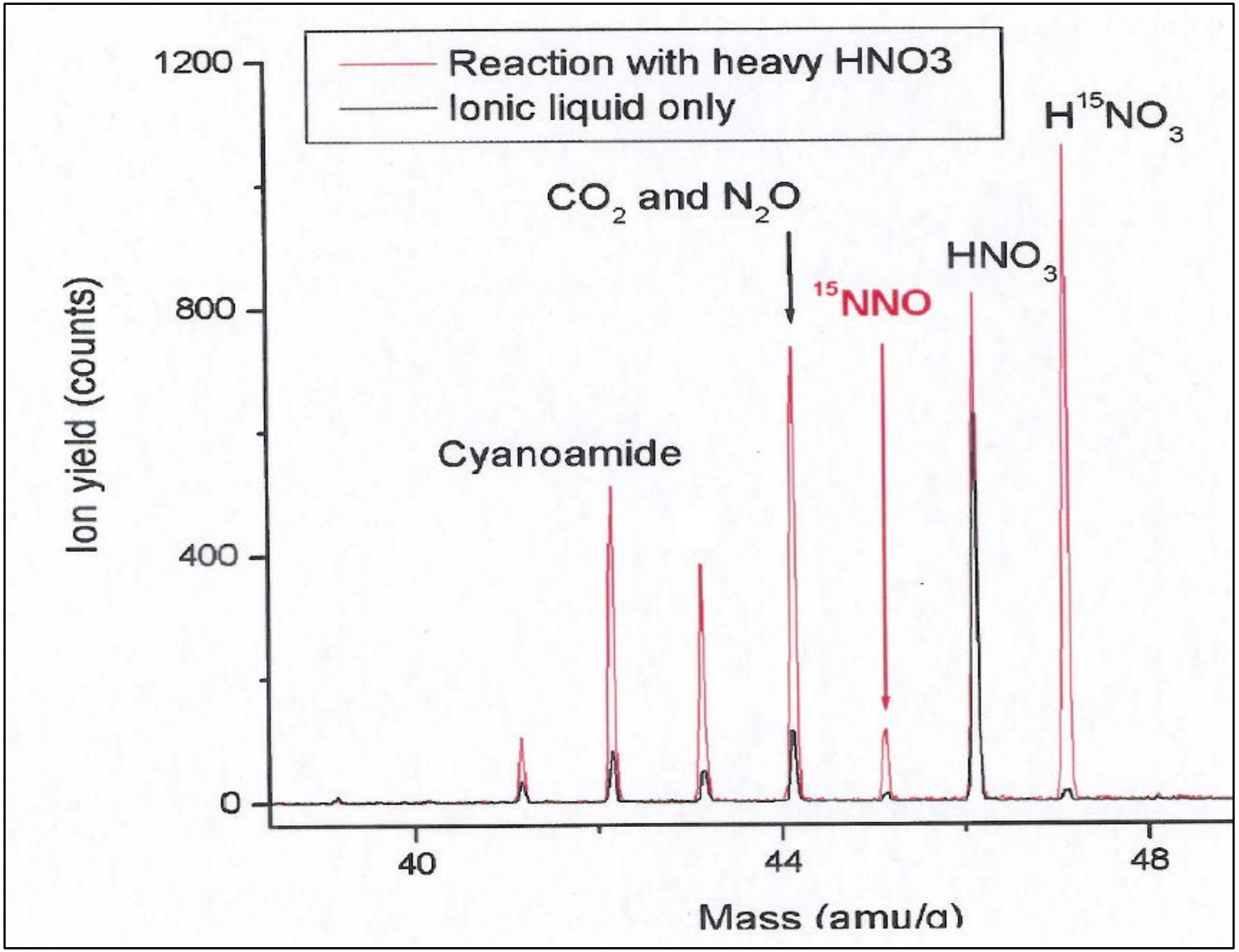
Experimental setup



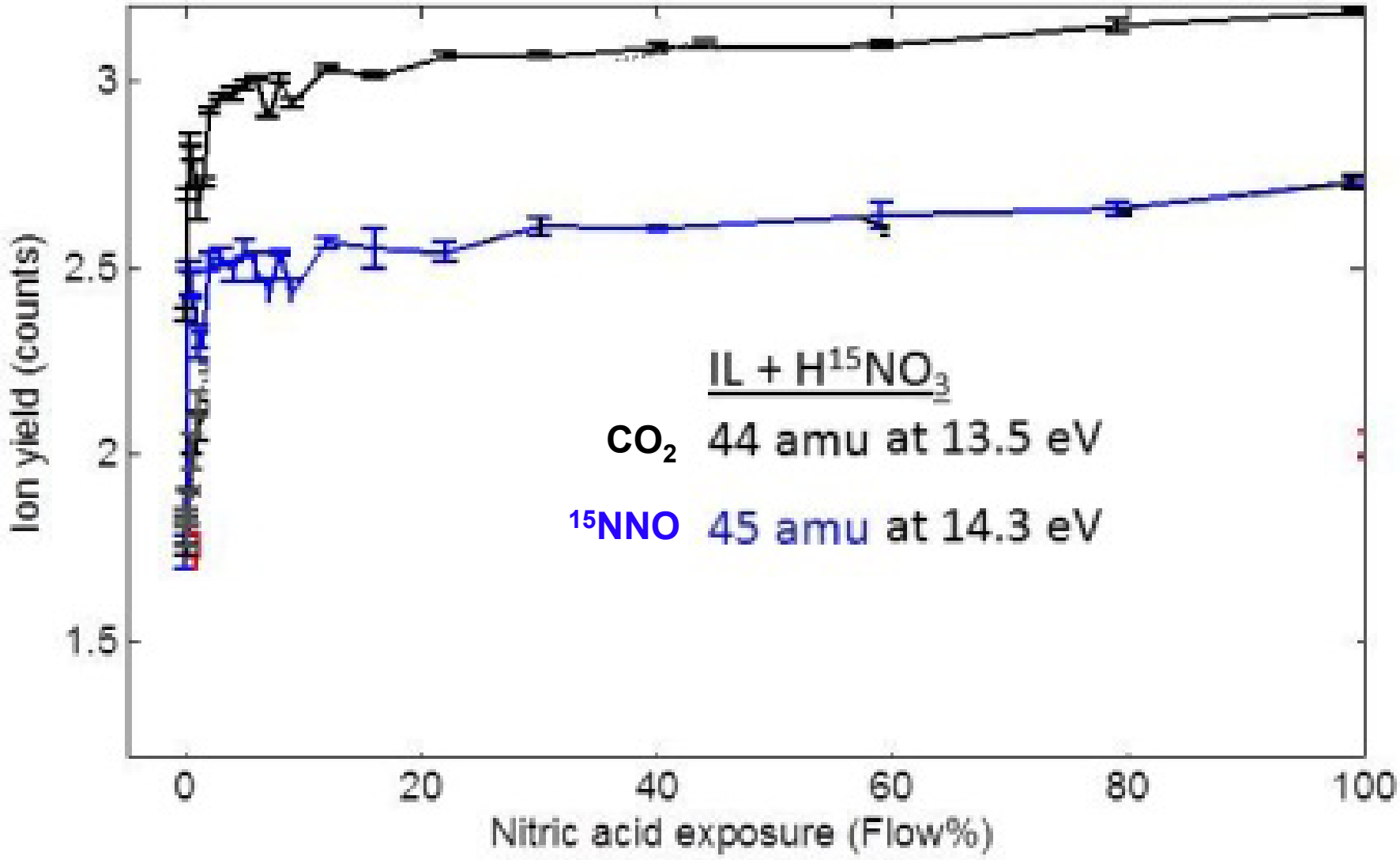
Identification of reaction products

- photoionization efficiency curve measured



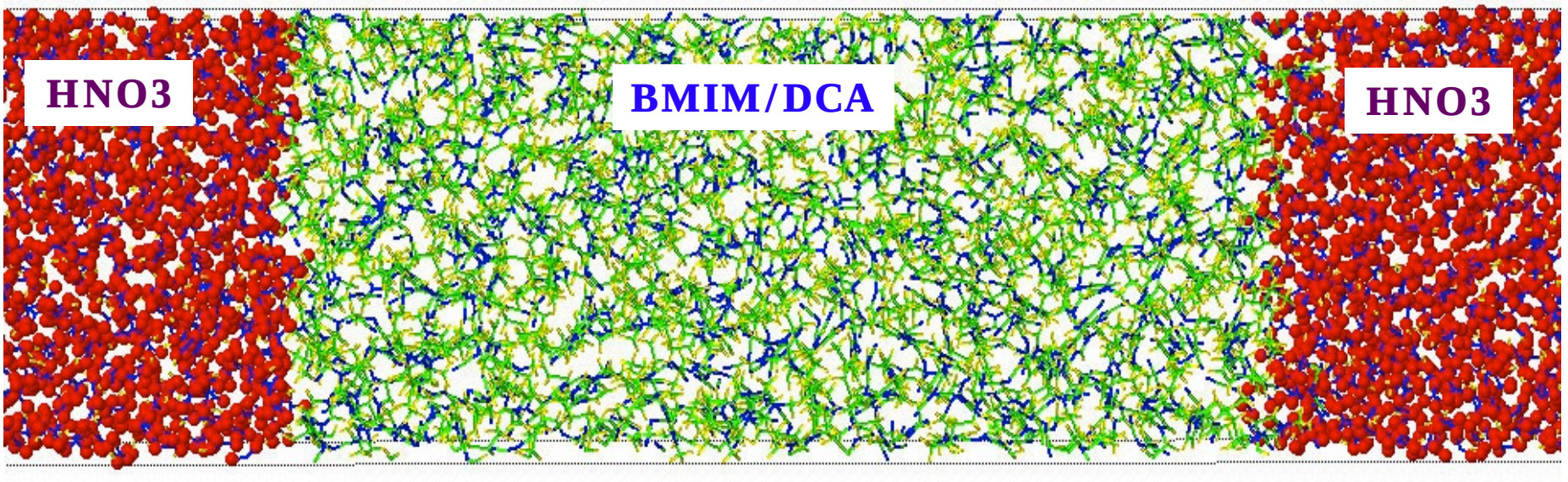

Reaction with heavy HNO3
Ionic liquid only
1200
800
400
0
Ion yield (counts)
$H^{15}NO_3$
CO_2 and N_2O
HNO_3
^{15}NNO
Cyanoamide
40
44
48
Mass (amu/q)

aerosol kinetics data

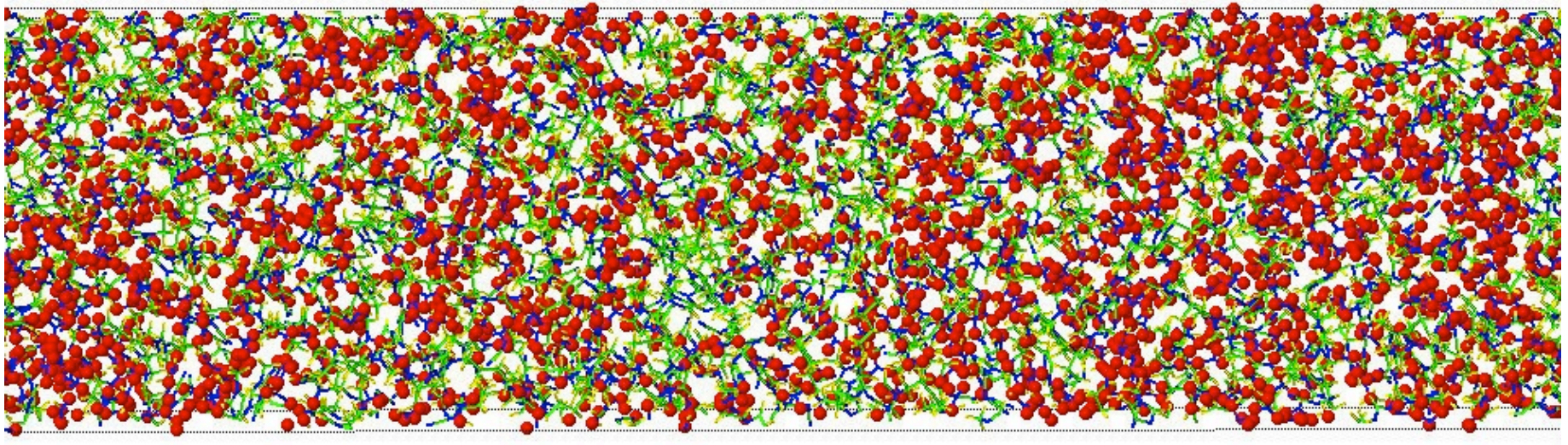


MD simulations of IL/oxidizer interphases: liquid-liquid

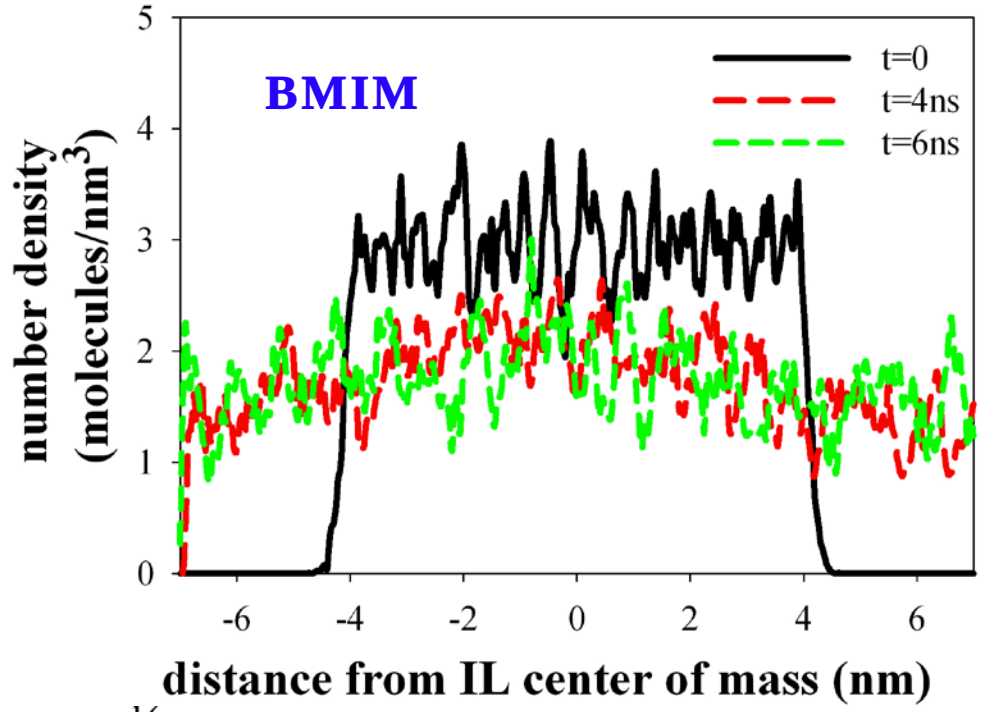
t=0

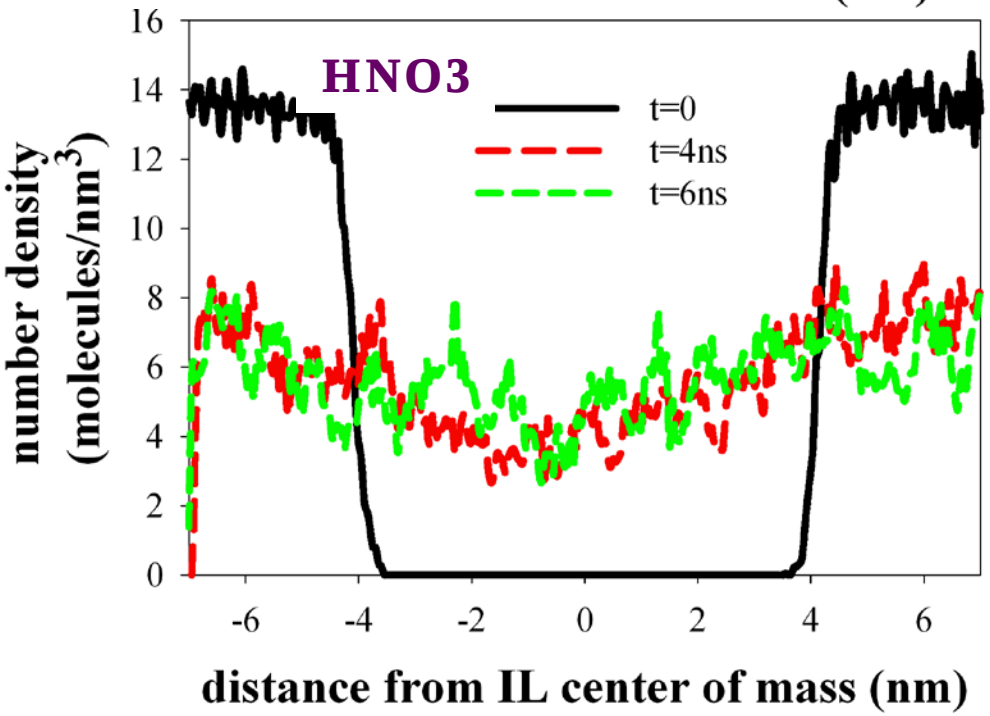


t=6ns



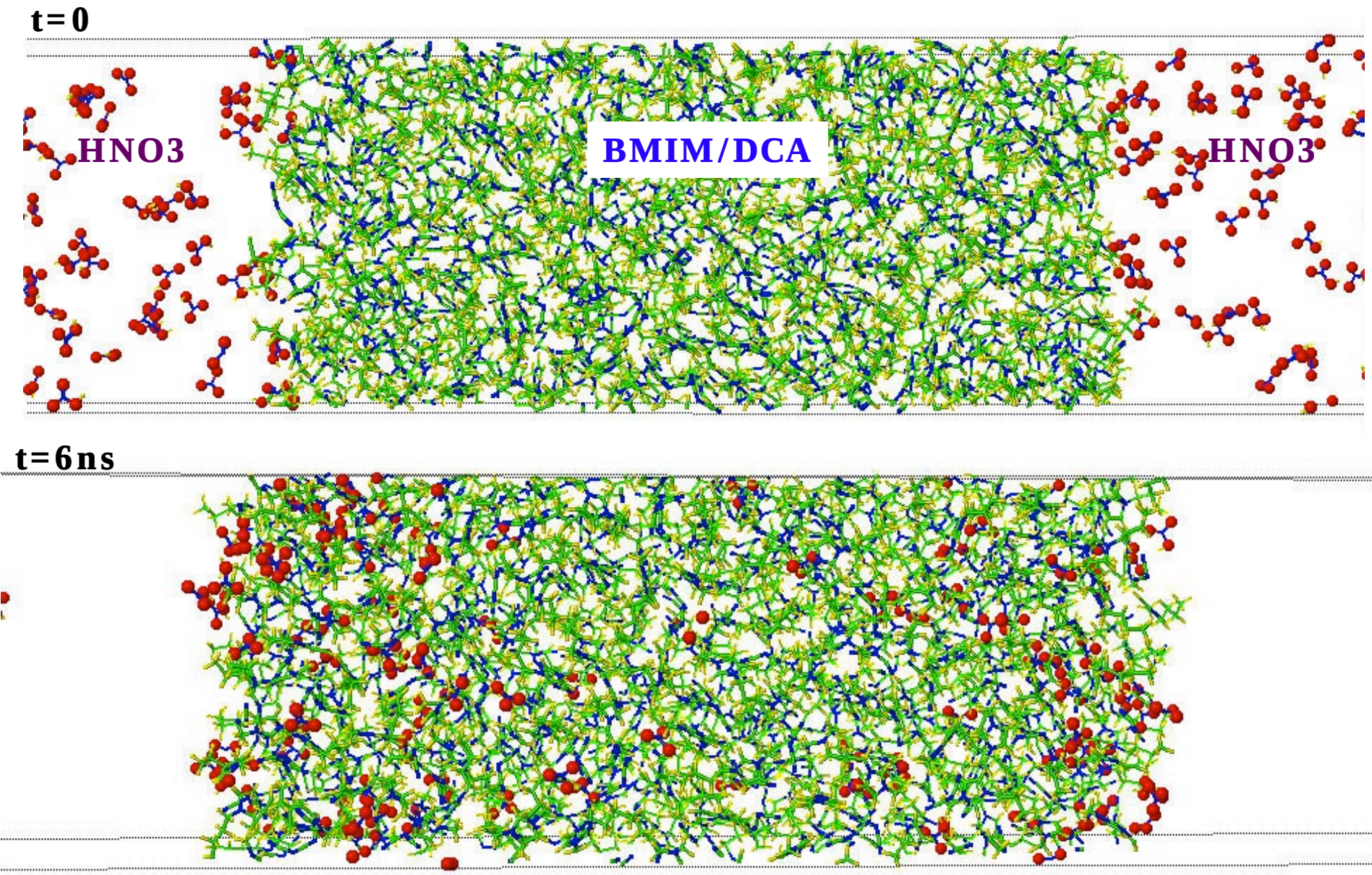
in liquid/liquid systems, mixing is rapid!

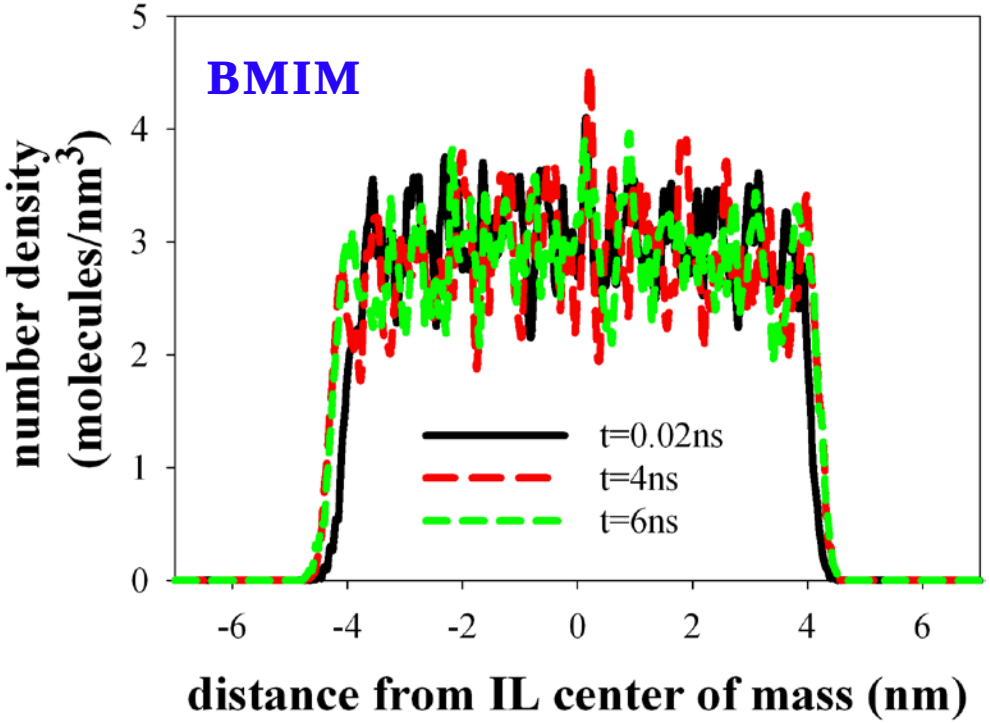


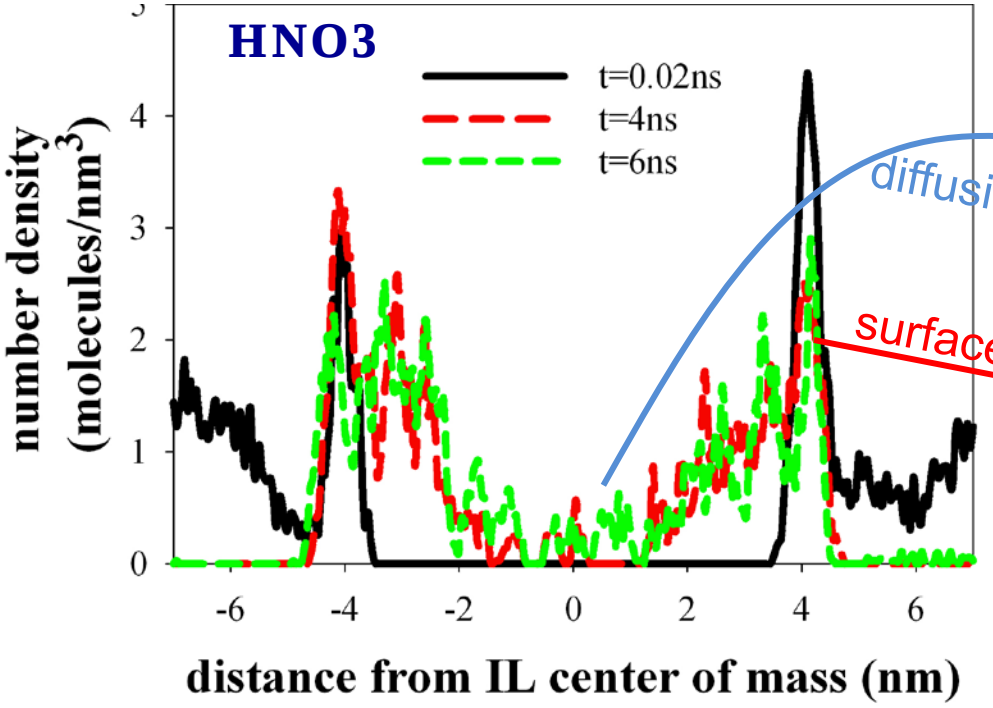


For the liquid-liquid interphase intermixing occurs fast (few ns time scale for investigated dimensions).

MD simulations of IL/oxidizer interphases: liquid-gas

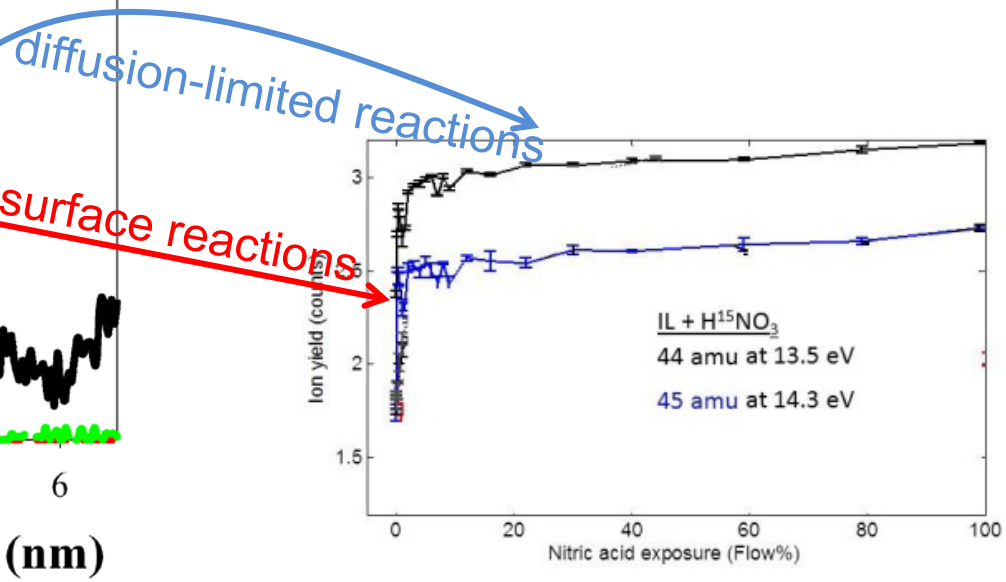






At the liquid-gas interphase HNO3 quickly adsorbs to the surface and then *slowly diffuses to the bulk.*

There is a certain concentration of HNO3 at the surface that system would like to maintain to *reduce the surface tension*



Conclusions

- Molecular dynamics can greatly improve our understanding of reactivity of ionic liquids:
  - ID thermal decomposition mechanisms
  - surface tension/diffusion limited processes
- Tunable VUV-PI-TOFMS a powerful experimental tool:
  - Direct detection of ion pairs upon vaporization
  - ID products my mass *and* ionization potential
  - Aerosols make ionic liquids more accessible by MS
- Design a better green rocket fuel with ionic liquids !!!

Acknowledgements

- Jianbo Liu
  (CUNY Queens College)
- Dmitry Bedrov
  (Wasatch Molecular)
- Schatz Group:
  - Scott Yockel
- Hase Group:
  - Swapnil Kohale

Mike Berman

- Leone Group
  (UC Berkeley and ALS):
  - Christine Koh
  - Amir Golan
  - Denisia Popolan
  - Oleg Kostko
  - Chris Harmon
  - Daniel Strasser
- Ionic Liquids Group
  (AFRL Edwards):
  - Gammy Vaghjiani
  - Jerry Boatz
  - Capt. Adam Schenk
  - Lt. Anna Sheppard

Questions?!

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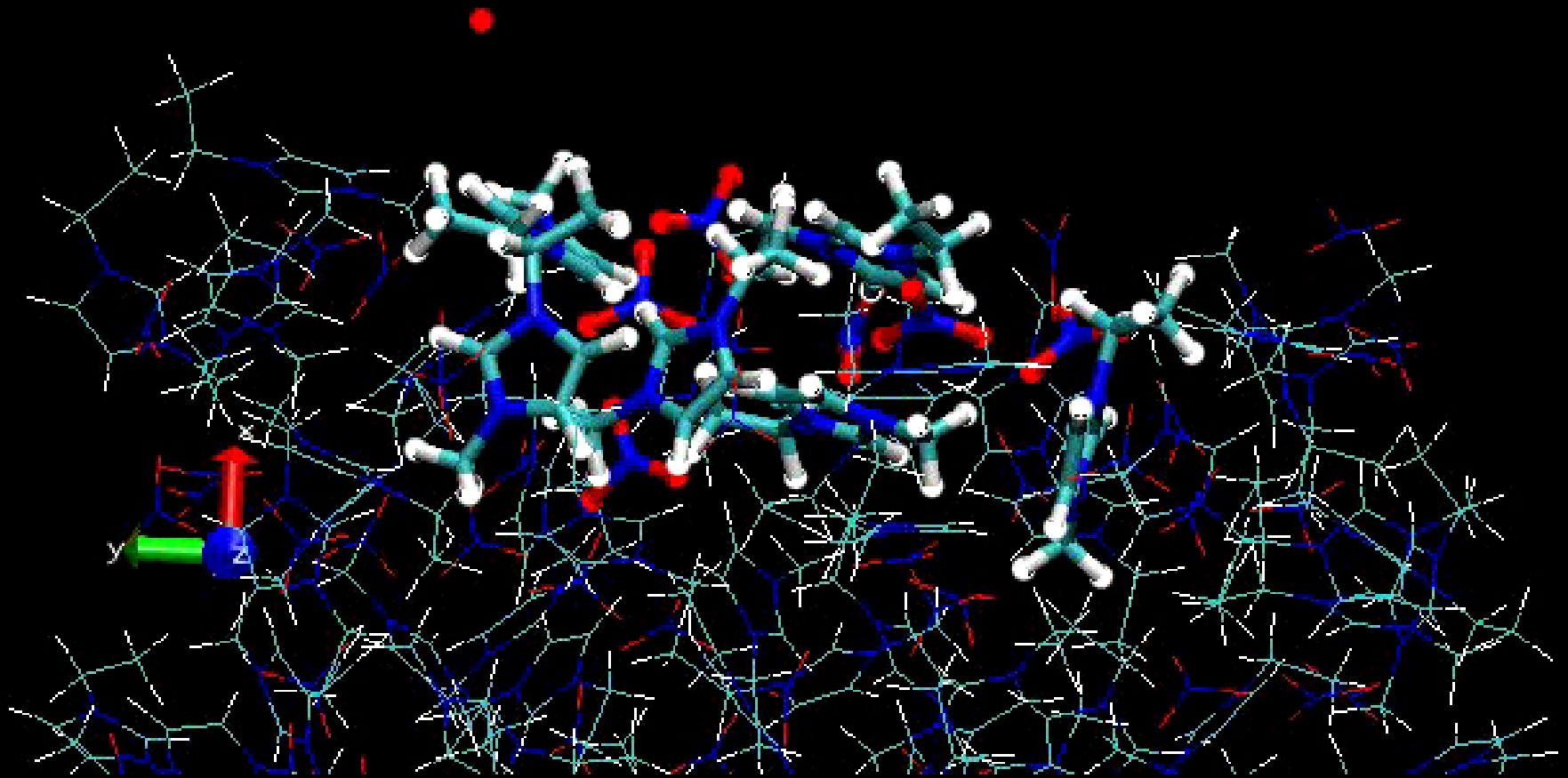
$O + EMIM^{+}NO_3^{-}$



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